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Acute and chronic risk assessment of BTEX in the return water of hydraulic fracturing operations in Marcellus Shale

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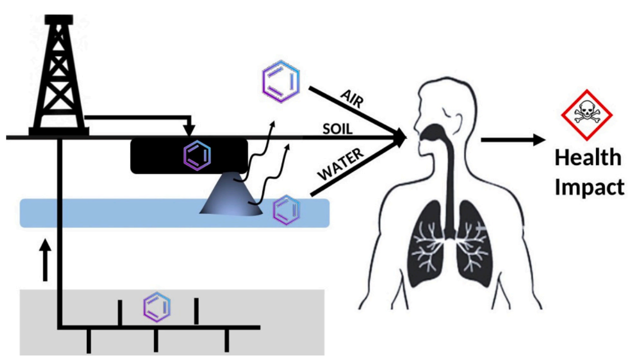
HIGHLIGHTS

- Pond leakage assessed for health risks via air, soil, water.
- Estimated time for corrective action before limit exceeded.
- Climate change impacts risk and main pathways.
- Children face higher health risk across time periods.

GRAPHICAL ABSTRACT



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ABSTRACT

Environmental pollution caused by human activities is a pressing issue in developed countries. In this context, it is vital to establish methodologies for the early and reliable estimation of the health risks posed by potential pollutants. Flowback and produced water (return water) from shale gas operations can contain toxic compounds, of which BTEX (benzene, toluene, ethylbenzene, and xylenes) are of concern due to their toxicity and frequent presence above regulatory limits. The return water generated by these operations is stored in ponds or tanks before reaching its final destination. Over time, the composition of this water changes, and leaks or inadequate contact can harm the environment and human health.

Here we developed a risk assessment framework to evaluate the temporal evolution of chronic and acute BTEX exposure risks caused by accidental return water leakage. We applied the approach to a hydraulic fracturing operation in the Marcellus Shale Formation. Starting with a time series of BTEX concentrations in the return water, our method deploys transport models to assess risk to health. Our approach compares exposure levels with regulatory limits for inhalation, ingestion, and dermal contact. By identifying the risk levels, exposure pathways, and control parameters in the case study for a range of periods after leakage, our study supports the implementation of appropriate risk mitigation strategies. In addition, by examining risk variation under arid, semi-

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arid, and humid climate scenarios, the study reveals the impact of climate change on soil characteristics and BTEX transport.

The development and application of this methodology is an important step in addressing concerns regarding shale gas operations. The approach proposed paves the way for sustainable practices that prioritise the protection of human health and the environment.

1. Introduction

An energy transition that ensures a guaranteed power supply requires a gradual abandonment of fossil fuels in line with the introduction of renewable energy sources. According to IEA (International Energy Agency) studies, natural gas demand is expected to increase by 3.5 % between 2021 and 2050 in the Stated Policies Scenario, with a corresponding rise in unconventional gas production of around 12 % over the same period (such production is estimated to increase by 162 % from 2010 to 2050) (IEA, 2022). Consequently, global onshore oil exploration is increasingly focusing on unconventional natural gas in shale formations (Han et al., 2021). The US and China are currently the leading producers of shale gas (Sun et al., 2021), with reserves of over $18.9 \cdot 10^{12}$ m^3 (He et al., 2014; Tan et al., 2019; Yazdan et al., 2020) and about $25–36 \cdot 10^{12}$ m^3 of technically recoverable natural gas, respectively (Ali et al., 2022; Shi et al., 2020).

The production of oil and gas from unconventional formations involves hydraulic fracturing technology, implying the injection of high-pressure water to cause a network of fractures. In North America, the average water use per well ranges from $11 \cdot 10^3$ to $17 \cdot 10^3$ m^3 (Shi et al., 2020), and this water contains between 0.5 and 2 % of additives and suspended solids. Subsequently, between 10 % and 30 % of the injected fluid returns to the surface as flowback and produced water (return water) (Bondu et al., 2021; Vazquez et al., 2014; Gregory et al., 2011). These waters have sparked significant controversy due to their potential environmental impact (Bonetti et al., 2021; Jiang et al., 2022). Given that the volume of return water decreases over time and its composition undergoes changes, it is necessary to consider the time factor in risk assessments (Kondash et al., 2017; Hayes, 2009).

Return water is commonly stored on-site in open-air, lined pits before transportation and treatment (Bloomdahl et al., 2014; Butkovsky et al., 2017). Various studies have indicated that most water quality issues associated with hydraulic fracturing activities in the US result from surface spills or leakage into shallow water formations (Gagnon et al., 2015; Gross et al., 2013; Sun et al., 2019; Veiguela et al., 2016; Vengosh et al., 2014; Yazdan et al., 2020). For instance, leaking storage and disposal wells around the Pavillion oilfield in Wyoming are responsible for the high concentrations of benzene, xylenes, gasoline range organics, and diesel range hydrocarbons found in the shallow soil of the area (Chen and Carter, 2020; Stephens, 2015; US EPA, 2011b).

Among the compounds present in return waters, BTEX (benzene, toluene, ethylbenzene, and xylenes) are of special interest for two main reasons. First, they are among the organic compounds most frequently detected in return water that are above detection limits (Luek and Gonsior, 2017). Groundwater samples taken in areas affected by spills indicate that BTEX concentrations exceeded their respective Maximum Contaminant Levels (MCL) in 90 % (benzene), 30 % (toluene), 12 % (ethylbenzene), and 8 % (xylenes) of the samples (Gross et al., 2013). Although these compounds are not necessarily components of the fracking fluids—which are increasingly environmentally friendly—, they have a geogenic origin and are thus present in return water (Luek and Gonsior, 2017). Second, BTEX compounds are highly toxic. In this regard, experimental studies have shown that acute and chronic exposure to benzene is associated with an increased risk of leukaemia and hematopoietic cancer (Heibati et al., 2017; Masekameni et al., 2019). Moreover, although toluene, ethylbenzene, and xylenes are not confirmed carcinogens, they can still damage the human nervous and reproductive systems, among others effects (Masekameni et al., 2019).

The main objective of this study is the development and implementation of a risk assessment framework that can be applied from the early stages of unconventional gas operations onwards. The framework is designed to assess both chronic and acute health risks to those engaged in shale gas exploitation (herein referred to as workers), as well as to local residents who might be affected by undetected leakage from return water storage tanks or ponds. This methodological approach can identify the BTEX compounds and exposure pathways most relevant to health risks and allow analysis of the temporal evolution of potential health effects as a function of time since the leakage of return water. By delving into the temporal evolution of health effects after the leakage, the framework facilitates a comprehensive analysis of the long-term consequences. To quantify these risks, the assessment relied on the calculation of hazard quotients for both carcinogenic and non-carcinogenic impacts.

Furthermore, we addressed the influence of varying climatic conditions on the outcomes. By conducting the analysis across media with differing characteristics—arid, semi-arid, and humid—we reveal the potential impact of climatic conditions on the results. The analysis of soil recharge conditions, which are shaped by climatic variations, provides valuable insight into how these conditions can influence the transport of BTEX compounds and therefore alter the potential health risks of these compounds.

To illustrate the application of this approach, the study uses data from wells in the Marcellus Formation. These data include BTEX concentrations within return water samples taken at various times after hydraulic fracturing.

In essence, this study seeks to enhance our understanding of the risks inherently tied to shale gas development. By identifying elements that could potentially surpass regulatory safety thresholds and gaining insight into response times, the approach can assist water management strategies, minimise environmental repercussions, and ultimately mitigate risks to the populace. This proactive knowledge will provide a valuable foundation for regulating and managing the environmental ramifications of shale gas operations.

2. Method and materials

Starting from a time series of BTEX concentrations in return water, the methodology proposed herein uses a succession of transport models that allow (from the initial data to the final receptor) an assessment of how BTEX present in return water may affect health. The models are used for the following: (1) to estimate the temporal evolution of BTEX concentrations in return water from time-series data of concentrations and over the operational lifecycle of horizontal hydraulic fracturing (Ma et al., 2018); (2) to estimate the evolution of BTEX concentrations in wastewater surface storage tanks (Ma et al., 2019); (3) to determine the evolution of BTEX concentrations in soil, through the vadose zone to the saturated zone or atmosphere, following a spill (Ma et al., 2019); and (4) to estimate the chronic and acute carcinogenic and non-carcinogenic risks to human health associated with different routes of BTEX exposure, namely air inhalation, soil inhalation, soil ingestion, soil dermal exposure, water ingestion, and water dermal exposure (US EPA, 1996a).

2.1. Starting data

The methodology is applied using data on BTEX concentrations published by the Marcellus Shale Coalition in a report by the Gas

Technology Institute (Hayes, 2009). This database provides the concentrations of the compounds detected in samples collected 1, 5, 14, and 90 days after hydraulic fracturing.

Of the horizontal hydraulic fracturing wells available, Well F, located in Washington County, Pennsylvania, is selected to test the methodology as it has data for all BTEX compounds for all the sampled days. The BTEX concentrations in the return water from this well are provided in Table S1 (Supplementary Material).

In addition, the methodology is also applied to the concentrations corresponding to the mean of the horizontal wells at locations C, D, E, G, K, and M taken from the Hayes report (Hayes, 2009). This value is referred to as "Mean Wells" throughout the paper and it is given in Table S2 (Supplementary Material). The results are presented for the scenario with the highest detected risk, thereby allowing a first estimation of the influence of BTEX concentrations on the level of risk. In addition, these results also allow an estimation of the relative risk of Well F compared to the entire field examined in the report issued by the Marcellus Shale Coalition (Hayes, 2009).

2.2. Return water models

Based on the abovementioned data, we can determine the temporal evolution of BTEX concentrations in return water, whose desorption kinetics can be fitted with a first-order two-compartment model, where each compartment is defined by its respective rate constants (Ma et al., 2018). In this model, the initial fast desorbing fraction (described by k_{fast}) occurs during the first few days after fracturing and it is associated with the flowback phase. This is then followed by a slower stage (slow desorption described by k_{slow}) associated with produced water, which can last for months or years (section S1 Supplementary Material). The evolution of return water volume can also be obtained by empirical expressions fitted to return volume data at different time points (1, 5, 14, and 90 days) available in Hayes (Ma, 2018). As a result, the two expressions allow us to obtain the evolution of BTEX concentrations in the storage pond and the impact of any leakage.

On average, the fast desorption phase makes the largest contribution to the BTEX concentrations in return water as there is a much higher volume of this water in this phase. As a result, the flowback phase makes the largest contribution to the evolution of the BTEX concentrations in the pond (Ma, 2018). Fig. S1 (Supplementary Material) shows a representative example of the temporal evolution of benzene concentration in the storage pond obtained from the models and Hayes' experimental data.

2.3. Transport models

Following leakage from a storage tank, the effluent is released into the unsaturated zone and then transported through it by various processes to finally reach the surface and the water table, thus affecting the various environmental compartments (López et al., 2008).

This evolution can be described using an analytical model that introduces a water table at a finite depth (Shan and Stephens, 1995). This model provides a one-dimensional solution (vertical direction) with an evaluation of transport in the aqueous and gas phases. Equations for the calculation of concentrations in the different media are given in section S1 (Supplementary Material). These equations are obtained under assumptions that are representative of a generic operation (Ma et al., 2019). This model is used to calculate the concentration of BTEX in the environment and allows the identification of the most relevant processes and parameters for the impact of BTEX on health.

Regarding atmospheric concentration, which is responsible for inhalation risk, volatile organic compounds are transported from the unsaturated zone to the atmosphere through several processes (Waitz et al., 1996). The model used allows us to directly derive the flux of pollutants reaching the atmosphere from solutions at the unsaturated zone-atmosphere interface.

Once at the soil-atmosphere interface, most BTEX molecules that reach the interface are vaporised towards the atmospheric boundary layer by diffusive transport mechanisms (Jiang et al., 2012). They then pass into the atmosphere where they mix and migrate with the wind (ASTM, 2015). In this last step, the assumption is made that BTEX compounds are completely diluted in the inhalation zone, leading to a constant concentration (Chen and Wu, 2007; Chen and Wu, 2009).

Regarding BTEX concentrations at the soil surface, these can be obtained directly from the analytical solution used by Shan and Stephens (Shan and Stephens, 1995) to study the evolution of the concentration profile in the unsaturated zone (section S.1.2 in the Supplementary Material). Once leakage occurs, BTEX compounds are adsorbed mainly on the solid phase due to the relatively high f_{oc} (fraction of organic content) in the vadose zone. Exposure to the soil surface (depth 0 m) can then occur by inhalation, ingestion, and dermal contact.

Finally, the model also allows us to estimate the BTEX flux through the water table to the groundwater. This flux is calculated at the vadose-groundwater interface directly from the expressions of Shan and Stephens (Shan and Stephens, 1995). The amount of pollutant deposited in groundwater over time is obtained from the integration of the above solution (see eq. S.15 in the Supplementary Material). The contaminant then undergoes various processes, including dilution with groundwater. Thus, as shown in eq. (1), the average concentration in the aquifer is calculated assuming that BTEX compounds entering through the water table are dissolved homogeneously throughout the volume of water available.

$$C_w = \frac{M_P}{V_{reservoir}} \tag{1}$$

where M_P is the amount of pollutant deposited in groundwater over time (Eq. S.41 in the Supplementary Material), and $V_{reservoir}$ is the volume of the aquifer in which the pollutant is diluted.

2.3.1. Concentration for acute exposure

To calculate the acute risk from inhalation and contact with water, the concentrations of BTEX compounds in water and inhaled air are calculated using the equations below (Eq. (2)).

$$C_{air\_surface} = K_H \cdot C_{water};$$

$$C_{\text{air\_inhalation}} = C_{\text{air\_surface}} \cdot \frac{D_{air} \cdot W}{V_{air} \cdot H \cdot d + D_{air} \cdot W} \tag{2}$$

where C_{water} (ppm) is the concentration of BTEX in return water, K_H is Henry's constant, V_{air} (m/s) is the wind velocity in the mixing atmosphere, H (m) is the vertical thickness of the mixing atmosphere, as well as the height for worker inhalation, d (m) is the thickness of the boundary layer, W (m) is the width of the source of contamination together with wind direction, and D_{air} (m^2/s) is the diffusion coefficient of the chemicals in the gas phase. The default parameters for calculating inhalation concentrations are shown in Table S4 (Supplementary Material).

2.4. Probabilistic exposure assessment

Here we assess the risks associated with chronic and acute exposure scenarios. Chronic exposure is relevant for those residing near unconventional gas operations who may be exposed to contaminants over several years (between 90 days and 30 years) (Goeden, 2018; Wattenberg et al., 2015). In contrast, acute exposure affects those working in shale gas developments (Wattenberg et al., 2015). In this case, we calculated the effects associated with exposure between 24 h and 30 days (Goeden, 2018).

For chronic risk assessment, the source of contamination is considered to be a wastewater storage facility releasing BTEX compounds into the air, groundwater, and soil as a result of leakage. For the estimations carried out herein, conservative criteria are applied from a risk management perspective. In this regard, it is widely accepted that the worst-case scenarios–in the context of oil spills in refineries and petrol stations—are those associated with leaks that go undetected for a long time. Therefore, the scenario considered here is that of an undetected leak over a lengthy period, which can lead to long exposure times, and whose impact on the results is estimated by a probability distribution that is sampled in the Monte Carlo simulations. Under the same principle, attenuation processes such as biodegradation or photodegradation are not considered. Consequently, we use a concentration ceiling to provide a conservative estimate of risk.

For this study, we consider that the return water is stored in a semi-buried tank, where a leak occurs in the underground section at a depth of between 50 and 150 cm. This scenario is deemed the most unfavourable for leak detection. With regard to the natural environment into which the water enters after leakage, the selection of parameters in an initial phase of risk assessment is not straightforward due to the scarcity of available data and/or the fact that the study is carried out in generic locations. In this regard, it is often necessary to resort to values from the literature that are considered representative of the study area (Troldborg et al., 2009). To this end, the water table is considered to be at a depth of 10 m from the surface (Gleeson et al., 2011). The values for soil bulk density (1.35 g/cm^3), porosity (0.5), water content (0.2), and organic content (0.0125) are obtained from the literature (see Table S4 in the Supplementary Material).

In addition, we deemed it of interest to determine the influence that processes related to climate change may have on risk to health. To this end, we considered a variation in recharge velocity that could cover a sufficiently wide range of environmental conditions in the area of the fracking operation. In this regard, we considered a variation of three orders of magnitude for the liquid advection velocity (V_L) (Szymkiewicz et al., 2019) in the soil. Thus, a V_L of 0.01 cm/day represents an arid zone, 0.10 cm/day a semi-arid zone, and 1.00 cm/day a humid zone. We used the concentration data under three environmental scenarios (arid, semi-arid, and humid) reported in the study by Ma et al. (2019).

The ambient concentrations of BTEX are calculated for the different scenarios indicated and with the values of the variables listed in Table S4 (Supplementary Material). The atmospheric concentration associated with the gas phase ($C_{air\_inhalation}$) is shown in Table S6 (Supplementary Material) for distinct recharge rate conditions and different times from the start of the leak. Likewise, the concentrations at the soil surface and the water table, also for different recharge rates and times since discharge, are shown in Table S7 and Table S8 (Supplementary Material).

To determine the influence of the dynamics of transport processes, risks for BTEX concentrations at 10, 10^2, 10^3, and 10^4 days after leakage are calculated for the different recharge rates. The volume of the underground aquifer is another aspect to be considered when making an initial assessment of the risks associated with contamination when the aquifer supplies drinking water. Here we used a generic aquifer with a volume of 44·10^3 m^3 (Abualfaraj et al., 2018). The aquifer volume is used to dilute the concentrations passing through the water table, assuming that the contaminant plume dissolves homogeneously throughout the water volume available, thus determining the contaminant concentrations reaching receptors. In the model used, the risk is proportional to the concentration and, therefore, inversely proportional to the dilution factor. Thus, the result can be extrapolated to other scenarios involving distinct aquifer volumes.

For acute toxicity, it is assumed that workers would be in contact with each type of pollutant for 1 or 15 days. The maximum concentration of each BTEX assessed in the storage pond is used conservatively for the calculations, assuming the same concentration for an acute risk at 1 and/or 15 days of exposure.

For the quantitative estimates, we considered that workers would not wear personal protective equipment (gloves/protective clothing). In the case of exposure to water, workers would have direct skin contact with return water as they would not be using such equipment (Durant et al., 2016) and, in the case of inhalation of the gaseous phase, they would be exposed because of the direct volatilisation of the return water.

Monte Carlo simulations with 10^5 iterations are performed to obtain probabilistic results. This approach allows uncertainties to be propagated through the assessment models, resulting in air and soil surface contaminant concentrations and health risk assessment through distinct exposure pathways expressed in terms of probability distributions. The values of the input variables used in the Monte Carlo simulation are listed in Table S5 (Supplementary Material).

2.4.1. Acceptable risk limits

The risk assessment took into account the Superfund Risk Assessment guidelines recommended by the US EPA. These establish the following three main exposure scenarios: (1) by ingestion, inhalation, and dermal contact through surface soils; (2) by inhalation of air; and (3) by ingestion, inhalation, and dermal contact through groundwater (US EPA, 2009, US EPA, 2011a). Acute exposure is assumed to be associated with dermal contact or inhalation pathways. Exposure scenarios via contaminated groundwater are not considered for these workers.

The risk assessment for the distinct exposure pathways is carried out using models developed by the US EPA (1996a). Both carcinogenic and non-carcinogenic risks (immunological, neurological, reproductive, etc.) are estimated. To this end, the models used for these calculations are presented in Table 1 and the input parameters used in the Monte-Carlo simulation are shown in Table S5 (Supplementary Material). In this regard, 10^5 iterations are performed for the modelling, and the results provide confidence intervals (5th and 95th percentiles) of the risk distribution. In addition, we conduct a sensitivity analysis of the results.

Table 1
Risk assessment models for the 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	$I_{soil-dermal} = \frac{C_S \times CF \times SA \times ABS \times ET \times EF \times ED}{BW \times AT \times 365}$
	Ingestion	$I_{soil-ingestion} = \frac{C_S \times IRS \times EF \times ED \times CF}{BW \times AT \times 365}$
Air	Inhalation	$I_{air-inhalation} = \frac{C_a \times IR \times ET \times EF \times ED}{BW \times AT \times 365}$
Water	Ingestion	$I_{water-ingestion} = \frac{C_W \times IR_d \times ET \times EF \times ED}{BW \times AT \times 365}$
	Dermal	$I_{water-dermal} = \frac{FA \times K_P \times C_W \times EV \times ED \times EF \times SA}{BW \times AT \times 365} \times \beta^{a}$ $\beta = \frac{t_{event} + 2\tau_{event} \times \frac{1+3B+3B^2}{(1+B)^2}}{1+B}$ $B = K_p \times \sqrt{MW/2.6}$ $\tau_{event} = \frac{I_{sc}^2}{6D_{sc}} = 0.105 \times 10^{0.0056 \times MW}$

C_s – surface soil concentration (ppm); $C_{air\text{-}inhalation}$ – inhaled air concentration (ppm); C_w – water concentration (ppm); $I_{soil\text{-}inhalation}$ – soil particle intake by inhalation, mg/kg-day^{-1}; $I_{soil\text{-}dermal}$ – dermally absorbed soil particle, mg/kg-day^{-1}; $I_{soil\text{-}ingestion}$ – soil particle intake by ingestion, mg/kg-day^{-1}; $I_{air\text{-}inhalation}$ – inhalation of air contamination, mg/kg-day^{-1};$I_{water\text{-}dermal}$ – dermally absorbed water, mg/kg-day^{-1}; and $I_{water\text{-}ingestion}$ – water ingestion, mg/kg-day^{-1}. Yearly exposure frequency (*EF* - d year^{-1}); Exposure duration (*ED* - year); Average time (*AT* - year); Bodyweight (*BW* - kg); Exploration time (*ET* – h d^{-1}); Inhalation rate (*IR* - m^3 h^{-1}); Ingestion rate (IR_d - m^3 d^{-1}); Ingestion rate (*IRS* - mg d^{-1}); Exposed skin surface area (*SA* – cm^2); Dermal absorption factor (*ABS*); Units conversion factor (CF – kg mg^{-1}); Particle emission factor (*PEF* – m^3/kg); Fraction of absorbed water (*FA* - dimensionless); Dermal permeability coefficient of a compound in water (K_p -cm/h); Event frequency (*EV* - event/d); Event duration (t_{event} – h/event); Lag time per event (τ_{event} – s/event); Molecular weight (*MW* – g/mol); Apparent thickness of stratum corneum (I_{sc} - cm); and Effective diffusion coefficient (D_{sc} – cm^2/h).

[a] (Durant et al., 2016).

The hazard quotient (HQ Eq. (3)) for non-carcinogenic effects and the carcinogenic risk (CR, Eq. (4)) for carcinogenic effects (Durant et al., 2016; US EPA, 2015) are used to determine whether the risks associated with each compound in the different exposure routes are acceptable. The *HQ* represents the ratio between the exposure results obtained from the risk models (I) and the reference limit value for chronic exposure (see Table S9 in the Supplementary Material). The value of the risk is considered acceptable if this ratio is <1.0 (Abualfaraj et al., 2018). *CR* is estimated by multiplying the obtained exposure (I) by a toxicity factor, *SF* (see Table S9 in the Supplementary Material). The US EPA sets an acceptable risk threshold for a *CR* value of 10^{-6} or less (Durant et al., 2016; US EPA, 2015).

$$HQ = \frac{I}{RfD}\ (oral);\ HQ = \frac{I}{RfC}\ (inhalation) \quad (3)$$

$$CR = I \times SF \quad (4)$$

where *RfD* is the chronic reference dose for oral exposure and *RfC* is the chronic reference concentration for inhalation.

Although individual risk factors are taken for each compound, a first estimate of the cumulative effect can be obtained by summing the individual risk values, assuming that their effect is additive but not synergistic (Gurjar and Mohan, 2003).

The results obtained can be used to facilitate the prevention of both carcinogenic and non-carcinogenic risks to human health through appropriate initial monitoring of return water and the implementation of remediation measures.

3. Results and discussion

This section presents the risks derived from the application of the methodology to the BTEX concentrations in the return water from Well F of the Marcellus Shale Coalition (Hayes, 2009), and therefore the numerical results are specific to this well. These results allow us to identify the main exposure pathways, their evolution over time, and how climatic conditions influence them, all based on the initial concentrations

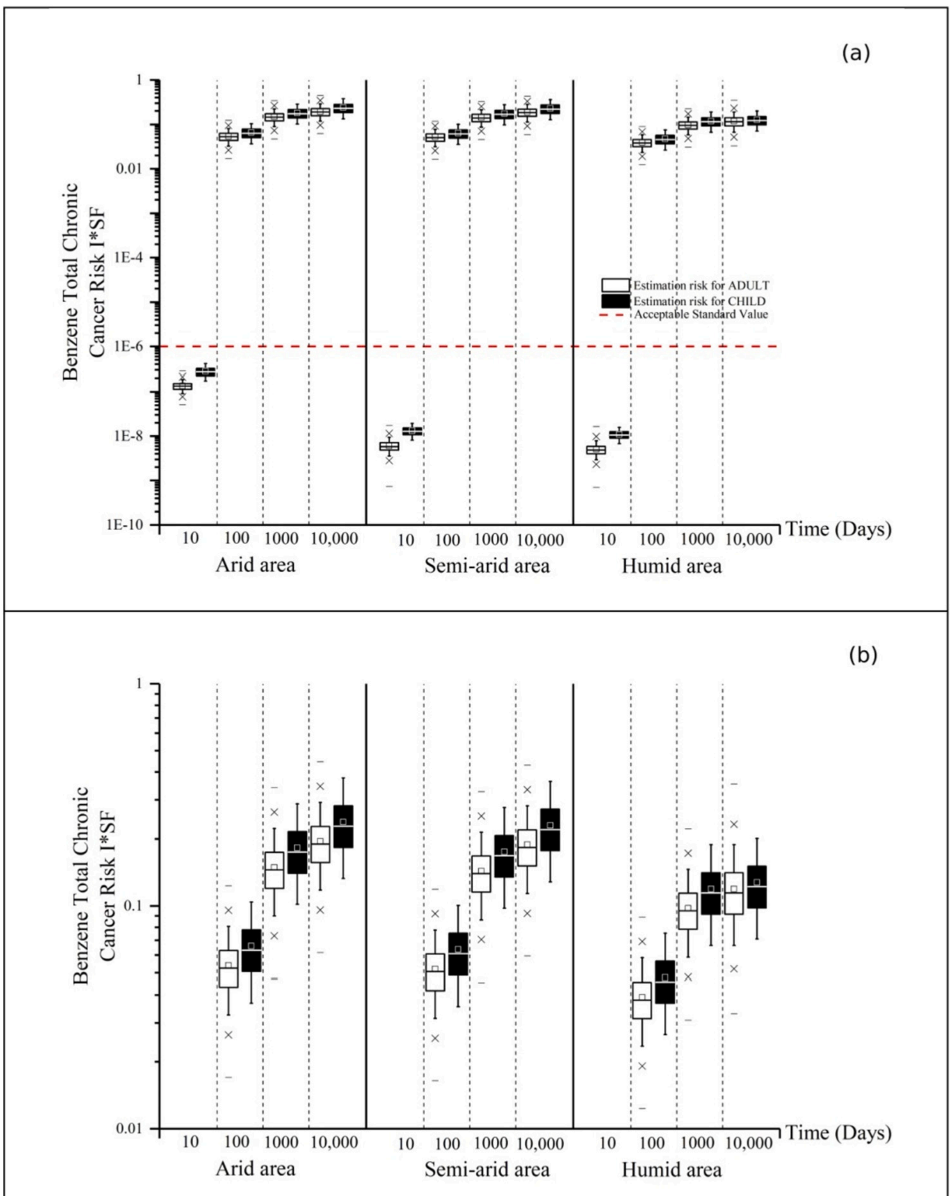

Fig. 1. (a) Chronic cancer risk results for benzene at 10, 10^2, 10^3, and 10^4 days after leakage. The black and white boxes indicate the exposure of children and adults, respectively. The red dashed line is the acceptable risk threshold for CR (10^{-6}). (b) Enlargement of the upper part of the risk shown in (a).

obtained from the return water. It is important to note that the results obtained are not necessarily representative of other shale gas plays, and that Well F is a specific case with high relative concentrations of benzene. Nevertheless, these results are interesting for the purpose of illustrating the scope of the methodology. However, to provide an initial estimate of the influence of BTEX concentrations in return water on the level of risk, the "Mean Wells" results are shown for the highest risk scenario (total benzene carcinogenic risk).

3.1. Chronic risk assessment

Exposure to BTEX poses carcinogenic risks associated with benzene, which is classified as carcinogenic to humans (IARC, 2011), and also a risk of developing non-cancer-related health problems, including respiratory, cardiovascular and/or endocrine diseases. These two results, obtained from the Monte Carlo simulations, are presented using box and whisker plots to show the uncertainty in the values. The boxes range from 25 % to 75 % and the whiskers from 5 % to 95 % of the result of the *HQ* or *CR*. The "–" types represent the minimum or maximum percentile and the "x" types the 5th or 95th percentile. The reference levels for carcinogenic and non-carcinogenic risks are 10^{-6} and 1, respectively, and are indicated by a red dashed line in the figures.

Figs. 1 and 2 show the *CR* and *HQ* values for children and adults, at different times after leakage, and for the three climate scenarios considered (arid, semi-arid, and humid). Fig. 1 shows the *CR* values for benzene while Fig. 2 shows the *HQ* results for each member of the BTEX group of compounds.

The figures show that only three months after return water leakage, the *CR* and *HQ* values for benzene substantially exceed the acceptable threshold under all the environmental conditions tested. Subsequently, approximately three years after the leakage starts, the risk levels tend to stabilise, a process associated with the diffusion/dispersion of BTEX in the environment.

Regarding the influence of climate scenarios, our results show that the lower the recharge rates, the higher the risk to residents, especially from about three months after the onset of the leakage, when thresholds are exceeded (Fig. 1b). These findings are consistent with the fact that we considered the scenario of a semi-buried wastewater storage tank and leakage below the surface. A higher recharge rate accelerates the migration of benzene to the water table, thereby reducing the concentration of this compound in the atmosphere, the main risk pathway (as can be seen in Figs. 3 and 4), thus reducing the risk to the population.

Finally, it should be noted that, despite the differences in the external environment and/or time since the release of the contaminant, all chronic cancer risks are higher for children than for adults. This finding is attributed to the increased inhalation and ingestion of contaminated exposure items, which may be related to the behaviour of younger children in the models.

With respect to the *HQ* values for toluene and ethylbenzene, these compounds show lower toxicity levels than benzene due to substantially lower reference concentrations for inhalation exposure (*RfC*) (see Fig. 2). Under all the scenarios analysed, the *HQ* values for ethylbenzene are consistently lower than the reference dosage ($HQ < 1$). Similar to the estimates for benzene, the *HQ* values for toluene and ethylbenzene are higher for children than for adults, and, over time, the *HQ* tends to increase until it approaches the threshold value. This threshold is exceeded for ethylbenzene, while for toluene the *HQ* value at 10^3 and 10^4 days may exceed the limit only in the case of exposure associated with children.

On the other hand, the behaviour of xylenes (see Fig. 2) shows similarities with that of benzene. The obtained for the first days after the leakage are at least seven orders of magnitude below the threshold level ($HQ \sim 10^{-7}$), increasing exponentially thereafter until the acceptable threshold is exceeded 100 days after the onset of the leakage ($HQ > 1$), and they tend to stabilise after 10^3 days.

Another important aspect to consider in the context of this work is the contribution of the different exposure pathways to the overall risk. Figs. 3 and 4 show the results of the *CR* and *HQ* assessment of the distinct exposure routes 10^4 days after the leakage of return water and for the semi-arid scenario ($V_L = 0.1$ cm/d). Accordingly, the inhalation route presents the highest risk in all cases. This result is attributed to the fact that the mechanisms of BTEX evaporation into the gas phase are more efficient than those of dissolution in water (Ma et al., 2019).

Thus, for the inhalation route, benzene and xylenes exceed the

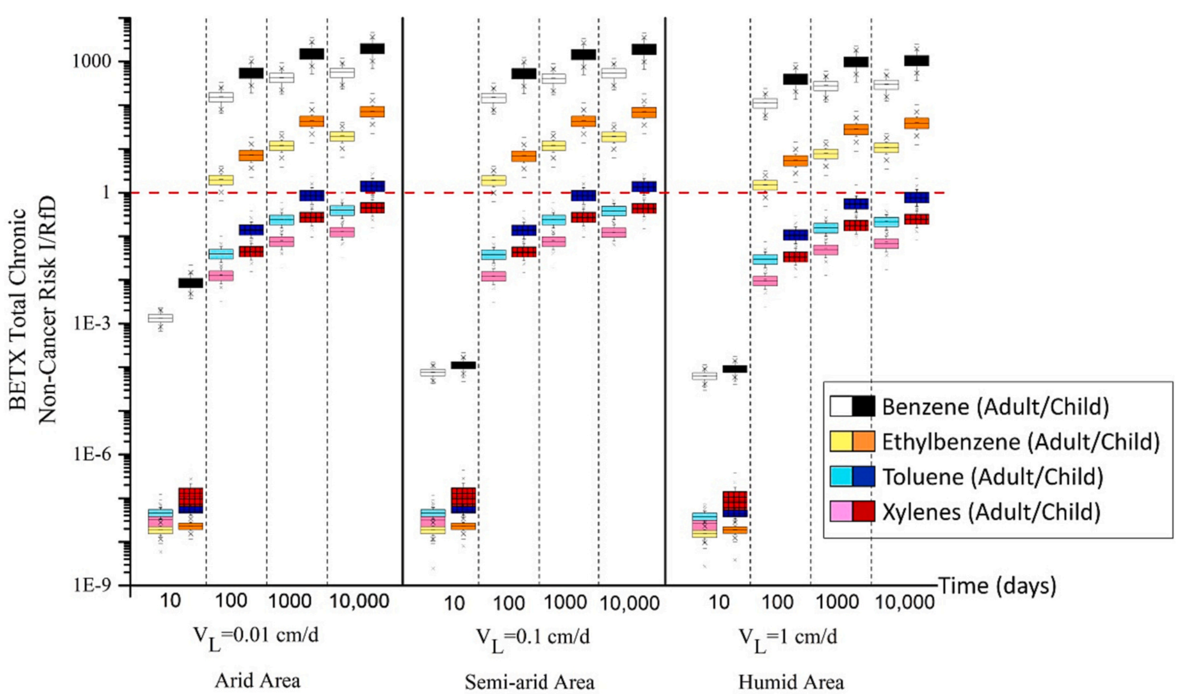

Fig. 2. Estimated non-cancer chronic hazard indices for BTEX at 10, 10^2, 10^3, and 10^4 days post-leakage. The red dashed line is the acceptable risk threshold for *HQ* (1.0).

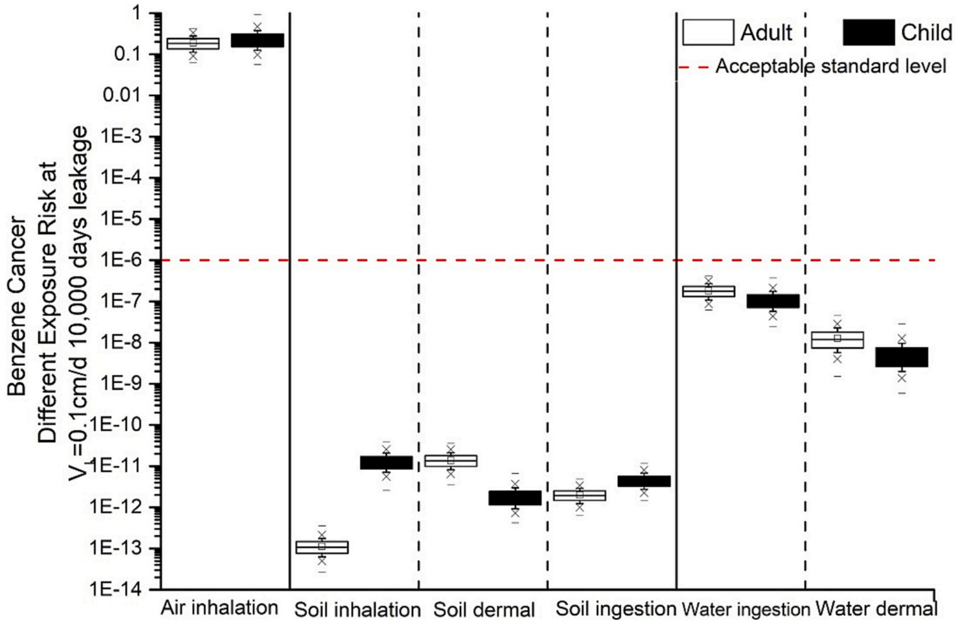

Fig. 3. Carcinogenic risk for different routes of chronic exposure to benzene after 10^4 days of leakage and at a V_L of 0.1 cm/d (semi-arid scenario). Black and white boxes indicate the exposure of children and adults, respectively. The red dashed line is the acceptable risk threshold for *CR* (10^{-6}).

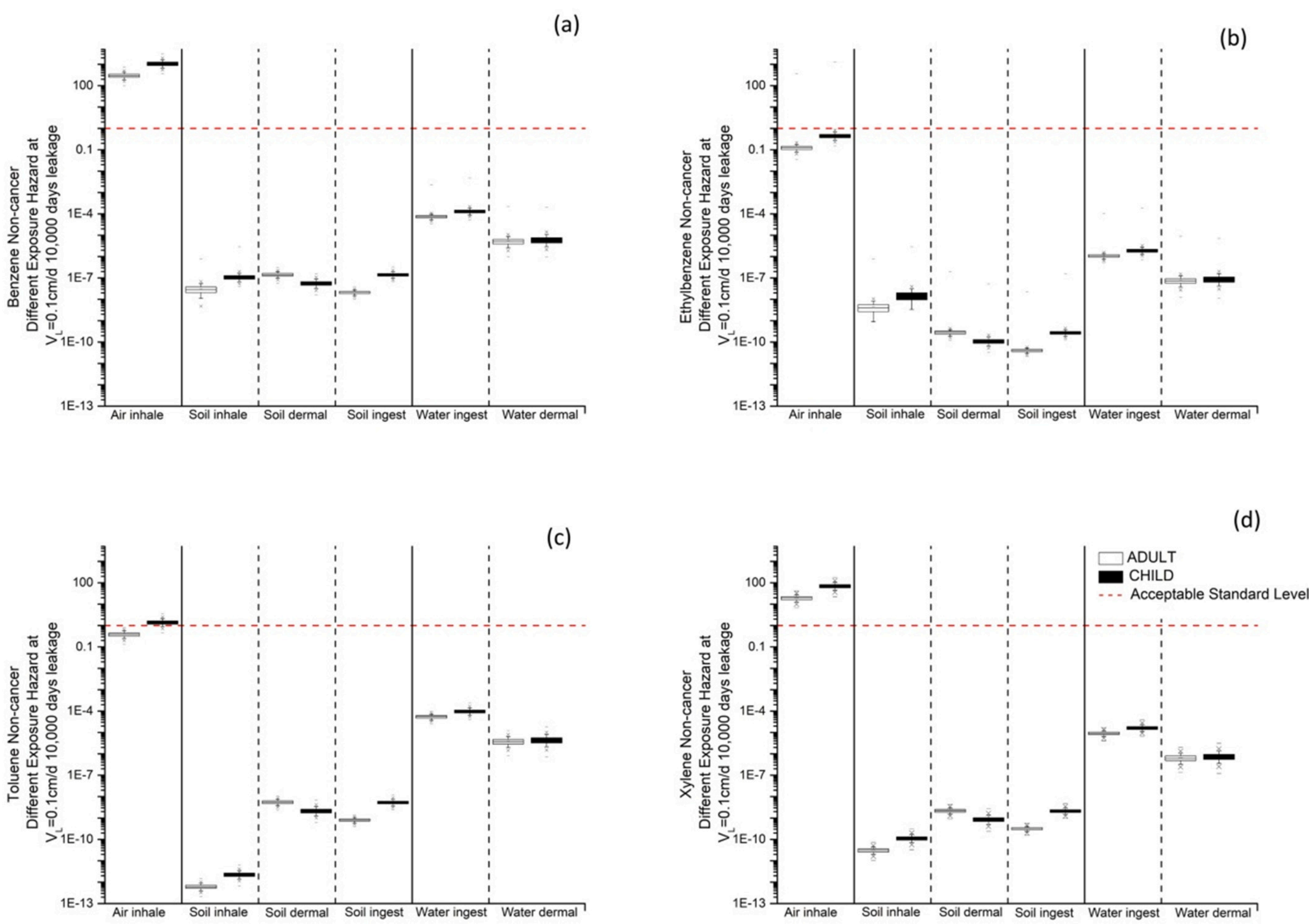

Fig. 4. Estimated results for the distinct routes of chronic non-cancer exposure to (a)-benzene, (b)-ethylbenzene, (c)-toluene, and (d)-xylenes, 10^4 days after leakage at a V_L of 0.1 cm/d (semi-arid scenario). Black and white boxes indicate exposure of children and adults, respectively. The red dashed line is the acceptable risk threshold for *HQ* (1.0).

threshold level for both carcinogenic (benzene) and non-carcinogenic risks. In contrast, the risk levels for ethylbenzene and toluene are acceptable, although for the latter the airborne exposure figures for children show that there is a 95 % probability that the *HQ* values are between 0.8 and 5.0, i.e. above the threshold, thereby indicating a potential health risk for this population. In fact, for all the BTEX compounds, the results indicate that children have a higher risk of exposure to air pollution. This result can be explained by several biological and behavioural factors. In this regard, children have a more vulnerable respiratory system and higher breathing frequency than adults, and they spend more time outdoors (Webb et al., 2016).

On the other hand, the carcinogenic and non-carcinogenic risk estimates associated with water, both by ingestion and dermal exposure, rank second and third in terms of highest impact, although they do not pose a serious health threat. The results for water exposure show that the reasonable upper limits of carcinogenic risk for adults and children (indicated by the 95th percentile of the probability distribution functions) are in all cases below the reference dose ($CR < 10^{-6}$) but not far from the threshold limit. These results highlight the need for continued vigilance and regular monitoring of water exposure scenarios. In all cases, the non-cancer risks are well below the threshold (more than three orders of magnitude).

In contrast to the carcinogenic risks, the non-cancer effects are more severe in children than in adults, although the threshold values ($HQ < 1$) are never exceeded. This result may be because carcinogenic risks are calculated as lifetime risks, i.e., the risk of developing cancer as a result of exposure to each compound over a lifetime of 70 years. In contrast, non-cancer risks are expressed in terms of the ratio of exposure to a reference value where the length of exposure is the same for adults and children, thus eliminating the influence of the time factor in the non-cancer risk formula. In addition, dermal exposure of children is generally considered to be greater than that of adults due to behavioural factors and also because children have a greater skin surface area per body weight. Therefore, the adverse effects of BTEX on children's health are magnified (Ginsberg, 2011).

Finally, the results of the Monte Carlo simulations for the exposure pathways to contaminated soil surface particles show that the *CR* and *HQ* results are in all cases well below the reference levels and that this exposure route poses the lowest risk. Among the different exposure scenarios to contaminated soil, our results indicate that the inhalation of soil particles poses the lowest risk. This finding is explained by the fact that surface particles are widely dispersed in the atmosphere (the particle emission factor value considered is 10^9 m^3/kg (US EPA, 1996b)), thereby greatly reducing the likelihood of inhalation. For inhalation and ingestion of soil particles, the cancer risk for children is higher than that for adults for the same reasons as stated above.

For the inhalation and ingestion of soil, the cancer risk for children is higher than that for adults for the same reasons as above. In contrast, regarding dermal exposure, the carcinogenic risk of benzene for children is slightly lower than for adults as the average skin area exposed and the duration of exposure for children is half and one-third of that of adults, respectively (US EPA, 2007).

The above results allow us to determine how external parameters, especially the liquid advection velocity, V_L, and the time since release ($t = 10$, 10^2, 10^3, 10^4 days) affect BTEX concentrations, and thus their potential impact on health. Probability functions of the risks associated with chronic exposure to BTEX (present in water, air, and surface soil by inhalation, ingestion, and dermal contact) allow estimation of whether these compounds compromise the health of adults and children living in the vicinity of unconventional gas operations.

To make a preliminary assessment of the differences that might occur between wells, a further application of the methodology is carried out using “Mean Wells” benzene concentration data in the return waters. The comparison between the results of Well F and “Mean Wells” is shown in Fig. 5. The trend is consistent as it is related to the behaviour of BTEX in the soil, although the level of risk is significantly lower due to the reduced concentration in the return waters.

3.1.1. Sensitivity analysis

We conduct a sensitivity analysis to determine how variability and uncertainty in the parameters of the exposure models influence the results. This approach allows us to rank the model parameters on the basis of significance. Benzene is used as a typical example for the sensitivity analysis of BTEX since only this compound poses a carcinogenic risk. Table S10 in the Supplementary Material shows the contributions of the various parameters, in both children and adults, to the risks (carcinogenic and non-carcinogenic) associated with the various exposure routes to benzene 10^4 days after the leakage and at a precipitation rate of 0.1

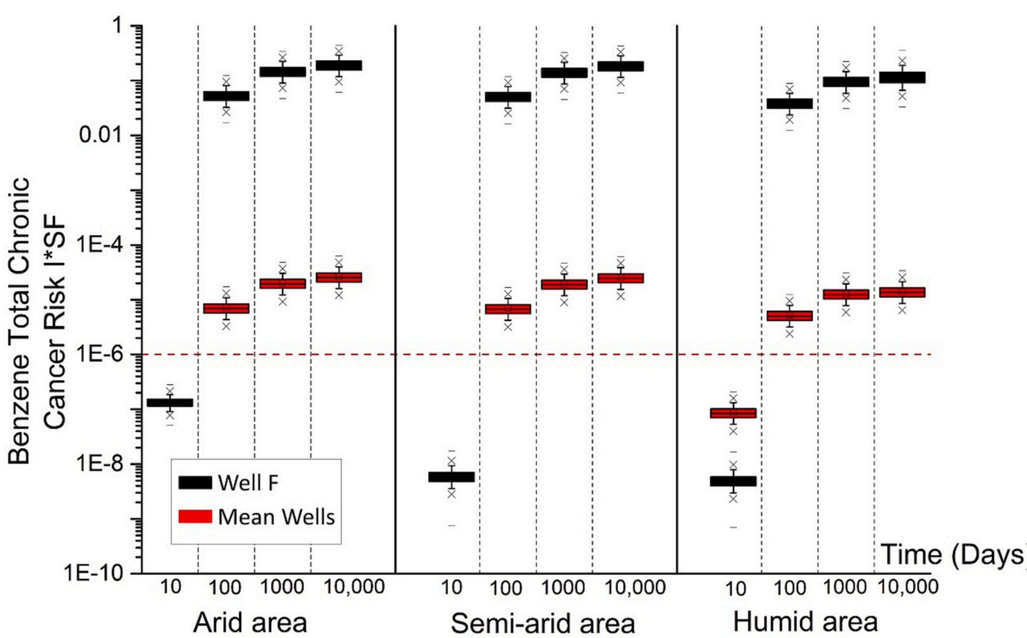

Fig. 5. Chronic cancer risk posed by benzene at different times after leakage. The black boxes represent the adult risk for F-well concentrations and the red boxes adult risk for “Mean Wells”. The red dashed line is the acceptable risk threshold for *CR* (10^{-6}).

cm/d.

For adults, concentration in the exposure medium and frequency of exposure are the most significant factors for the following routes: inhalation associated with air and soil contamination; ingestion associated with soil contamination; dermal exposure associated with soil contamination; and ingestion associated with water contamination. For the dermal exposure associated with water pollution, duration of exposure is the most influential factor (approximately 27 % for non-cancer risk and 25 % for cancer risk), followed by frequency of the event (about 26 % for non-cancer risk and 24 % for cancer risk), exposure concentration (about 17 % for non-cancer risk and 15 % for cancer risk) and exposure time (about 16 % for non-cancer risk and 14 % for cancer risk).

For children, the most significant factor is body weight for inhalation exposures associated with air and soil contamination, and ingestion for exposure associated with soil and water contamination, for both carcinogenic and non-cancer risks. Regarding dermal exposure associated with water pollution, the frequency and duration of contact are the most influential parameters for both carcinogenic and non-carcinogenic risks, as in the case of adults. Finally, for dermal exposure of children to soil, the average skin area exposed is the most influential variable for the route of dermal contact, followed by body weight.

3.2. Acute risk assessment

To assess the acute risk to workers, we identified the most relevant pathways associated with shale gas extraction operations and estimated the impact associated with them. These results can be used to help identify the control measures needed to reduce risk to an acceptable level (Reichwaldt et al., 2016). For this assessment, the acute exposure scenario assumed that a worker constantly inhales contaminated air and has direct dermal contact with return water through hand contact. It is assumed that the worker does not use adequate protective equipment and the maximum reported concentrations of BTEX are conservatively used for the risk estimation at 1 and 15 days of exposure. The BTEX concentrations in air used for the acute risk calculation are given in Table S11 in the Supplementary Material.

Figs. 6 and 7 provide estimations of the acute carcinogenic risk associated with benzene and the acute non-carcinogenic risk associated with BTEX for inhalation exposure. These estimates allow the identification of the most significant health risk and can facilitate the implementation of mitigation measures to reduce or eliminate that impact (McKenzie et al., 2012).

The inhalation carcinogen risk index (*CR*) for 1 day's exposure at each of the four accessible concentrations (for 1, 5, 14, and 90 days) ranges from $5{\cdot}10^{-6}$ to $5{\cdot}10^{-5}$, and for 15-day exposure between $5{\cdot}10^{-5}$ and $5{\cdot}10^{-4}$. All confidence intervals for the *CR* obtained are above the threshold limit value (10^{-6}), regardless of the exposure duration and initial concentration (Fig. 6).

In terms of non-carcinogenic hazards (Fig. 7), all 15-day exposure results for benzene and xylenes are above the threshold ($HQ > 1$). With regard to the results for 1-day exposure, the hazard indices for benzene are above the acceptable level for the 5-day concentration and slightly below the threshold for the rest, while for xylenes the threshold level is exceeded only for the 90-day concentration. For ethylbenzene and toluene, the hazard indices are in all cases below the acceptable levels. They are associated with lower *RfC* values than benzene and xylenes, thereby implying less toxicity.

Workers exposed to such conditions would benefit most from wearing protective equipment, particularly for respiratory protection.

The acute risks, both carcinogenic and non-carcinogenic, for dermal exposure to BTEX do not exceed the risk threshold in any case (section S6 in Supplementary Material). The results indicate that the likelihood of carcinogenic or non-carcinogenic effects on health is negligible. The small surface area of skin contact and the frequency of exposure probably explain this observation. These factors greatly reduce the prospect of exposure to doses significant enough to induce an adverse physiological response, at least in short-term exposure scenarios.

3.3. Discussion of the results

The paper addresses the importance of adequate risk assessment in unconventional gas-producing environments, particularly with respect to BTEX compounds.

The above results illustrate the existence of wells with BTEX concentrations that lead to exposures exceeding regulatory threshold limits. They therefore have the potential to pose a significant health risk to adults and children living close to unconventional gas fields and their workers. Furthermore, these results offer insights into the evolution of risk over time and how it might be influenced by shifts in environmental

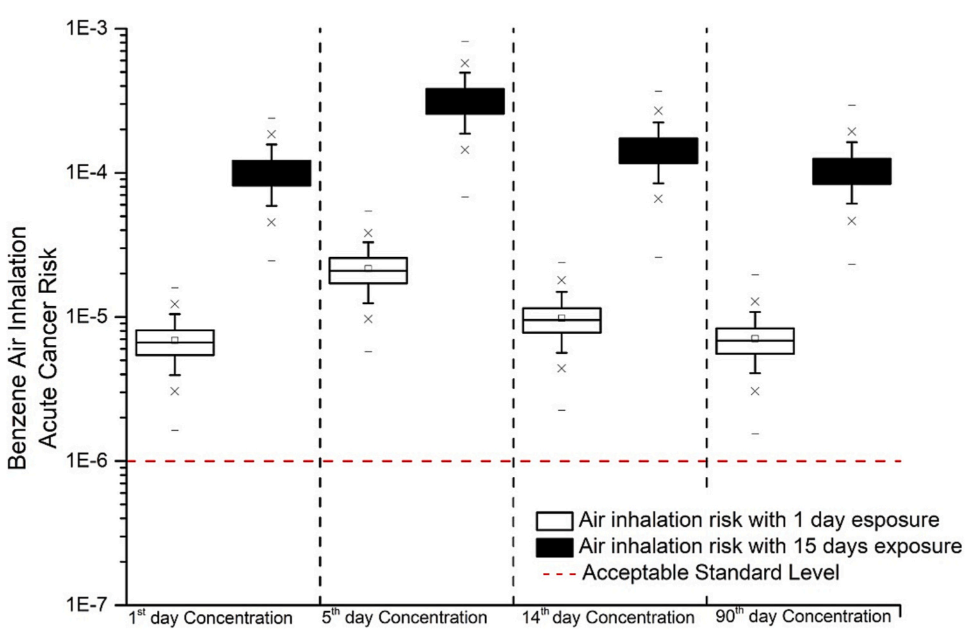

Fig. 6. Estimated cancer risk from acute exposure to benzene. The white and black boxes indicate the cancer risk for 1 and 15 days of exposure, respectively. The red dashed line is the acceptable risk threshold for *CR* (10^{-6}).

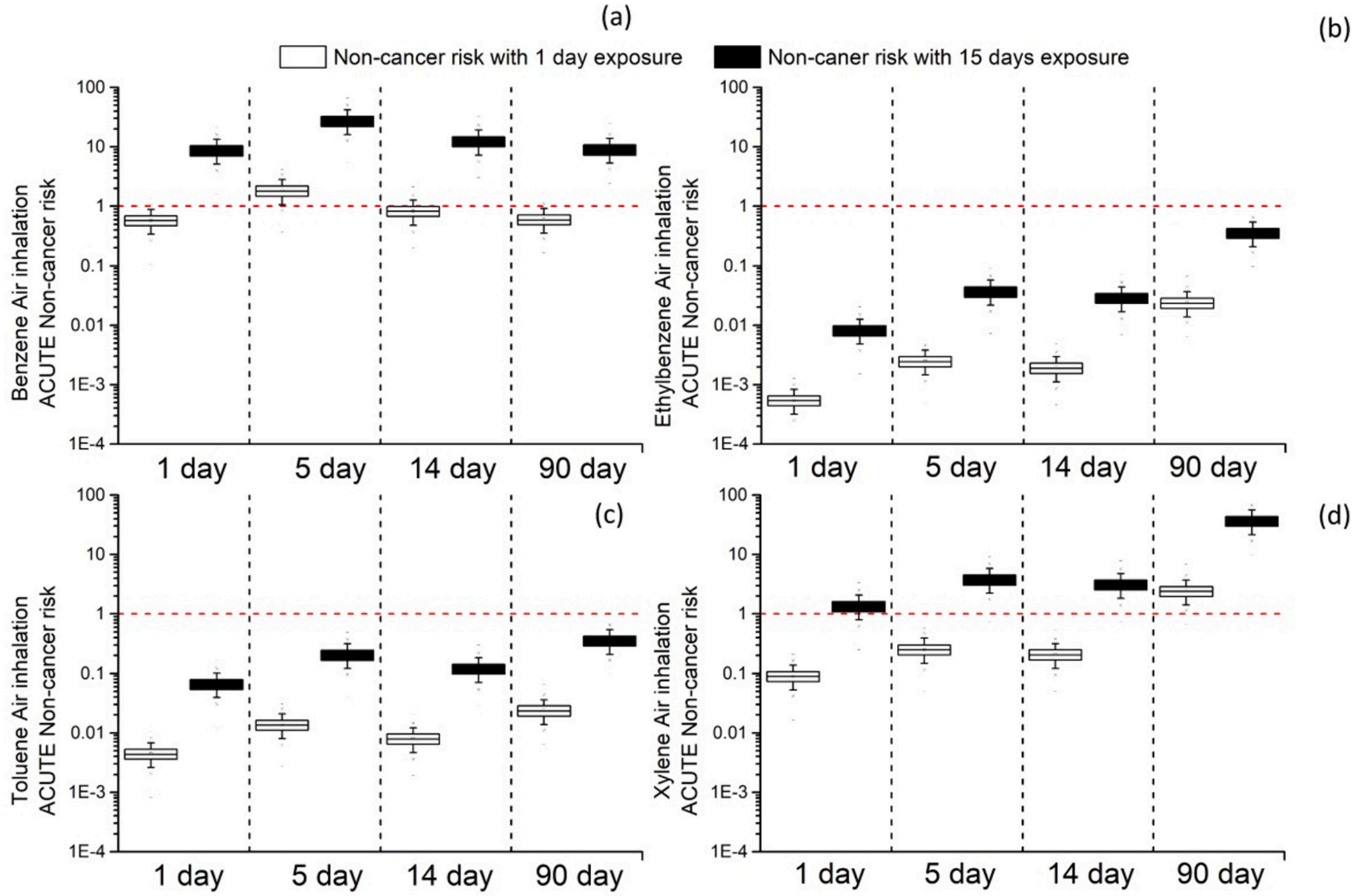

Fig. 7. Non-cancer hazard quotients for acute exposure associated with inhalation of (a)-benzene, (b)-ethylbenzene, (c)-toluene and (d)-xylenes. The white and black boxes indicate 1- and 15-days exposure, respectively. The red dashed line is the acceptable risk threshold for *HQ* (1.0).

conditions, represented by the parameter V_L, which is linked to climate alterations. Importantly, the applicability of our methodology does not depend on the availability of detailed data. Designed to be implemented in the early stages of shale gas exploitation, the methodology has a single prerequisite, namely the collection of return water samples at varying intervals after hydraulic fracturing in order to determine the concentrations of BTEX present (or any other relevant compound family).

The results show that climate change has the potential to influence the evolution of health risk by altering key variables within distinct environmental components. In particular, in the context of a shift towards drier conditions, the significance of risks associated with the atmosphere will intensify. Conversely, wetter conditions will increase the relevance of risks associated with water. The methodology reported herein facilitates the estimation of shifts in primary risk pathways, contingent upon the results of climate models applied to the specific geographical area of operation.

The results provided by the methodology therefore support proactive safety analyses, enabling the formulation of preventive measures. Primarily, in the context of return water leakage and remediation, the methodology can estimate the timeframe available for intervention across diverse impacted environmental components before threshold limits are surpassed. From a strategic standpoint, the output from this initial analysis plays a pivotal role in determining effective strategies for the management of storage ponds on a well-by-well basis. Such strategies would ensure that BTEX concentrations consistently remain below thresholds considered harmful to human health. In this regard, such strategic management would significantly curtail associated operational risks.

Of note, the probability of a leakage from a return water storage tank or pond should not be overlooked when performing a risk assessment. This probability can be methodically established through a casuistic approach, relying on the statistical scrutiny of failures in operational shale gas fields. Such an approach may encompass variables like the characteristics of the shale gas reservoir, year of construction, and the regulatory framework in the shale gas production zone. The evaluation of these aspects will allow a comprehensive assessment of the likelihood of leakage.

Additional factors to enhance the assessment could include the following: 1) exploration of alternative aquifer mixing models; 2) incorporation of exposure pathways linked to the consumption of locally produced animal and plant products, thus broadening the scope of potential risks; 3) research into potential synergistic effects arising from the various compound families considered in ecotoxicity studies; and 4) implementation of a methodical examination of exposure times, involving adjustments to density function parameters. This approach would facilitate the determination of the timeframe after which permissible concentrations of given compounds might be exceeded.

4. Conclusion

On the basis of our findings, we can draw the following conclusions:

- Atmospheric pathways are the most relevant sources of risk, and in the case study, both carcinogenic and non-carcinogenic risks associated with benzene and xylenes exceed acceptable thresholds on multiple occasions.
- Children are at greater risk than adults, despite significantly shorter exposure times.

- Sensitivity analyses highlight the significance of contaminant concentration in the results. Conducting these initial risk assessments for any shale gas exploitation would enable proactive adjustment of return water management based on inferred concentrations from model application, thereby minimising the risk to the population in the event of accidental leaks.
- Climate change can alter soil properties, such as recharge rate, which plays a crucial role in contaminant transport through the vadose zone. Depending on the location of the shale gas exploitation and expected climate evolution, risks may shift towards atmospheric or groundwater pathways as the climate shifts towards drier or wetter conditions.
- Regarding the time factor, in the case under consideration, the initial movement of BTEX in the vadose zone after a leak is slow, and therefore the exposure associated with any contamination would take around 100 days to exceed the limit values. This temporal insight is highly relevant in the context of remediation strategies.

In summary, using data from the early stages of shale gas exploitation, the methodology described herein enables the prediction of BTEX concentrations, exposure pathways, and duration of exposure that could harm health. The methodology emerges as a comprehensive tool for risk management and decision-making in the context of unconventional gas operations.

CRediT authorship contribution statement

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

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.167638.

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