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The passive sampler assisted human exposure risk characterization for tetrachloroethene soil vapor intrusion scenario

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ABSTRACT

The potential human health risks associated with soil vapor intrusion and volatile organic compounds (VOCs) exposure were characterized at an industrialized site by the quantification of gaseous VOCs in soil pores using a passive sampling technique. The gaseous tetrachloroethene (PCE) in soil pores varied between 12 and 5,400 μg m^{-3} showing 3 orders of magnitude variation with dependence on groundwater PCE concentrations. Though the PCE concentration in the air only varied between 0.45 and 1.5 μg m^{-3} showing negligible variations compared to the variation observed in soil pores. The PCE concentration in the air varied between 0.45 and 1.5 μg m^{-3}. The calculation of fugacity suggested that the PCE in the test site originated from groundwater. Measured PCE in groundwater ranged from 14 to 2,400 times higher than PCE in soil gas. This indicates that conducting a vapor intrusion risk assessment using passive soil gas sampling is critical for accurate risk characterization and assessment. Estimated PCE inhalation cancer risks for street cleaners and indoor residents varied between 10^{-6} and 10^{-4} with a low plausible hazard, and between 10^{-3} and 10^{-2} with a high risk, respectively. The results of this study demonstrate that passive sampling offers a significantly lower cost and labor-intensive approach compared to traditional methods for assessing pollution distribution in contaminated sites and characterizing risks. This highlights the potential for wider application of passive sampling techniques in environmental studies.

1. Introduction

Volatile organic compounds (VOCs) which can be originated from fuel combustion, storage outflows, and fuel spills are ubiquitous pollutants in soil and groundwater (Alharbi et al., 2018; Feng et al., 2020; Huang et al., 2014). They can migrate from the subsurface to buildings in a process known as soil vapor intrusion. Soil vapor intrusion is the most critical VOCs migration pathway for exposure to contaminated soil and groundwater (Bekele et al., 2018; Rivett et al., 2011; Soucy and Mumford, 2017). Exposure to VOCs through inhalation poses health risks to humans (Belpomme et al., 2007; Chang and Chen, 2008; Petry et al., 2014). To protect against VOC exposure, the potential risks related to soil vapor intrusion were evaluated. When the measurement of soil gas is unavailable, the groundwater concentration can be used to evaluate soil vapor intrusion (EPA, 2015). However, groundwater concentration is not recommended for evaluating vapor intrusion because of uncertainties related to partitioning and transport (EPA, 2015). Several studies have shown that VOCs in soil gas are the most important factors in soil vapor intrusion risk assessments (Ma and Lahvis, 2020; Ma et al., 2020). Therefore, accurate quantification of VOCs in soil gas and risk assessment based on measurements are critically important to understand intrusion risks and design risk management strategies.

Active sampling methods, such as Tedlar bags and canisters, are typically used to detect VOCs in soil gas, because of high accuracy and competence for short-term monitoring concerning episodic high pollution (ASTM, 2006). However, problems related to vacuum and flow in

Abbreviations: ADD, average daily dose; AT, average lifespan; BW, body weight; ED, exposure duration; EF, exposure frequency; ePTFE, expanded polytetrafluoroethylene; ET, exposure time; HI, overall non-carcinogenic risk associated with exposure to a specific threshold pollutant; IR, inhalation rate; MW, molecular weight; PCE, tetrachloroethene; PDMS, polydimethylsiloxane; RFC, non-carcinogenic reference concentration for toxic pollutants; TOL, toluene; VOCs, volatile organic compounds; XYL, *p*-xylene.

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low-porosity soils and leak prevention can occur (Gschwend et al., 2022). Active sampling is also inappropriate for long-term monitoring due to fluctuation (Seethapathy et al., 2008). Although VOCs in soil gas can be estimated from the soil content of VOCs assuming equilibrium (MEE, 2014; ME, 2015; Ma and Lahvis, 2020), inaccuracies in predicting VOCs in soil gas have been observed in many studies (Swartjes, 2011; Zhang et al., 2018). Because soil gas sampling is recommended for soil vapor intrusion risk assessment (EPA, 2015), passive sampling can be used. Passive sampling, which operates on the molecular diffusion of chemicals and detects episodic contaminant fluctuations through long-term monitoring, can resolve the problems associated with active sampling (Kot-Wasik et al., 2007; Ouyang and Pawliszyn, 2007; Seethapathy et al., 2008). In addition, passive sampling is convenient and inexpensive to use (Liang et al., 2021; Salim and Górecki, 2019).

The potential human health risks associated with soil vapor intrusion and exposure to VOCs at industrialized sites need to be characterized. In this study, a passive sampling technique was used to quantify gaseous VOCs in soil pores. A contaminated site with VOCs around Iksan National Industrial Complex (35°56′33″N 126°58′29″E), Iksan, Republic of Korea, was selected for the study. Industrial complexes were first established in the 1970s. Since then, the Iksan Industrial Complex has become a leading industrial complex in the Republic of Korea. Therefore, this area is surrounded by many manufacturing plants. Various industries, such as textiles, electronics, and chemicals, are concentrated in this area and contributed significantly to the contamination of the site (Ambade et al., 2022; Sankar et al., 2023).

To monitor the distribution of VOCs at contaminated sites, VOCs in the groundwater and air were measured. The fate of VOCs was estimated by calculating their fugacity in air and soil. The potential human health risks associated with soil vapor intrusion were assessed by measuring VOCs in soil vapor. For assessing VOCs in soil gas, a passive sampler that had been developed in a previous study specifically for measuring VOCs in soil vapor was employed. (Moon et al., 2023). This study is a novel application of passive sampling to characterize the risk of soil vapor intrusion. The vapor intrusion attenuation factors, which were determined through empirical methods by the USEPA, were employed to calculate the indoor air concentrations of VOCs (EPA, 2015; Guidance for Supplementary Vapor Intrusion, 2020). By utilizing projected indoor VOC concentrations and actual outdoor measurements, the assessment of both cancer and non-cancer risks associated with inhalation was conducted for individuals working within buildings close to a pollution source, including laborers, and environmental beautification workers.

2. Materials and methods

2.1. Monitoring wells

For target VOCs, toluene (TOL), tetrachloroethene (PCE), and p-xylene (XYL) were chosen and bought from Sigma-Aldrich (Milwaukee, WI, USA). Table S1 lists the material properties. Monitoring wells A, B, C, D, E, F, and G were deployed at 35°56′24″N 126°58′34″E, 35°56′26″N 126°58′40″E, 35°56′33″N 126°58′40″E, 35°56′40″N 126°58′38″E, 35°56′41″N 126°58′28″E, 35°56′33″N 126°58′29″E, and 35°56′33″N 126°58′35″E. Fig. 1 shows the locations of the deployed monitoring wells. Monitoring wells F and G, which are approximately 150 m apart, are denoted as F1 and G1, respectively. The hole diameter of the monitoring wells was 120 mm. The inner and outer diameters of the well casing were 50 mm and 120 mm, respectively. The well depth was 50 m, and the filter pack was composed of SiO_2. The seal is made of bentonite. Groundwater from the monitoring wells was extracted using a pump (Supertwister pump, Proactive, USA) in April 2022. After purging the volume of monitoring wells twice, 1 L of groundwater was extracted by 2~3 L m^{-1}. The VOCs concentrations of groundwater were analyzed by GC–MS. Details of the analyses are shown in the Supplementary Materials.

2.2. Soil gas sampling

Polydimethylsiloxane (PDMS) (ID 0.5 mm × OD 1 mm), widely used as a passive soil sampler, was selected as the model polymer (Kim and Kwon, 2020; Kim et al., 2017, 2022; Moon et al., 2023). In order to prevent direct interaction between the soil and PDMS, a 25 mm piece of PDMS was placed inside tubes made of 50 mm expanded polytetrafluoroethylene (ePTFE) (obtained from Huizhou Besteflon Industries Co. Ltd.) which is inert. These tubes had an inner diameter of 2 mm and an outer diameter of 4 mm, and they were designed to allow the passage of gases exclusively. The PTFE caps of 2 mm diameter were used to seal. The details about the previously developed sampler are shown in Moon et al. (2023). Passive samplers were inserted into a 60 mm sampler holder, which had 28 holes for penetrating gas, and then sealed with a 15 mm stainless steel circular cone cap for deployment in soil and a 500 mm stainless steel cylinder holder with a diameter of 5 mm, as shown in Fig. S1. At the contaminated site, most of the surface was paved with asphalt and concrete; therefore, 10 soil-exposed sites were selected for soil gas sampling where trees were planted for street landscaping. Fig. 1 shows the sampling sites. Selected tree beds are close to the deployed groundwater monitoring wells within 10 m horizontally. For QA/QC, a control site without contamination has been selected in a natural park in Sejong City (36°60′91″N 127°28′20″E), which was 150 km away from the contaminated site. For each site, three passive samplers were deployed in surface soils (<50 cm) at horizontal intervals of 10 cm in April 2022, as shown in Fig. S2. After 10 d, VOCs in the passive samplers, PDMS, were extracted with a solid adsorption tube made of Tenax (Tenax-TA® tubes, KnR, Republic of Korea) for 24 h. Solid adsorption tubes were extracted and analyzed using TD-GC MS (APK 2350, Shimadzu, Japan). Details of the analyses are provided in the Supplementary Materials. The

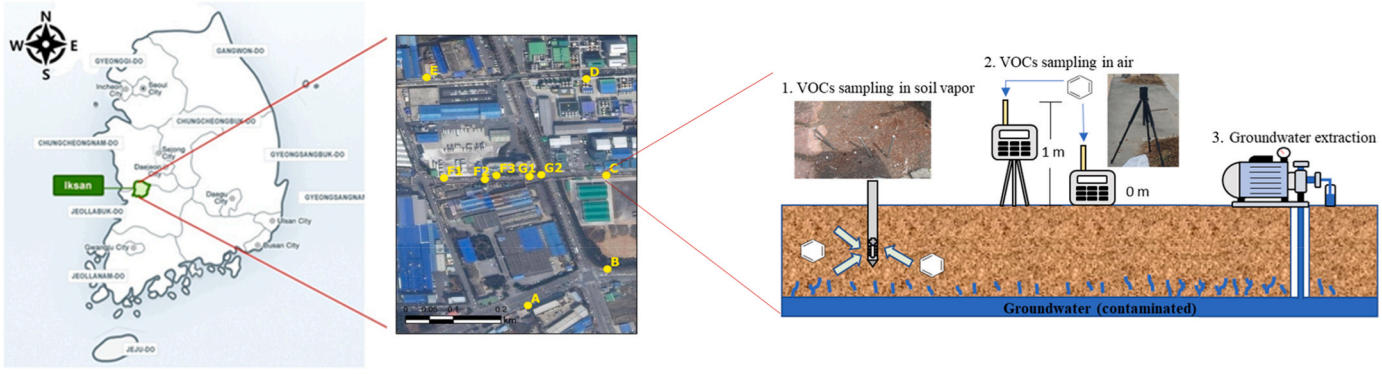

Fig. 1. Yellow dots in the map represent sampling sites around Iksan National Industrial Complex, Iksan, Republic of Korea. Figure stands for procedures of field tests in contaminated sites.

concentrations of VOCs in the soil vapor were calculated as follows:

$$C_g = K_{pdms} C_{PDMS} \quad (1)$$

Where C_g (μg m^{-3}) is the concentrations of VOCs in soil vapor, K_{PDMS} is the predetermined equilibrium partition coefficient of VOCs between PDMS and gas (Moon et al., 2023), and C_{PDMS} (μg m^{-3}) is VOCs in PDMS.

2.3. Air sampling

VOC concentrations in the air at 0 and 1 m above the soil ground selected for passive sampling were measured with active sampling. The solid adsorption tube made with Tenax (Tenax-TA® tubes, KnR, Republic of Korea) was used for sorbent. A low-volume air sampler (MP-Σ30KN Mini Pump, Taewon Sibata, Republic of Korea) was used to sample air at 1 L min^{-1} for 10 min. Solid adsorption tubes were extracted and analyzed using TD-GC MS (APK 2350, Shimadzu, Japan).

2.4. Risk assessments

The term 'cancer risk' represents the potential for cancer to develop due to exposure to a probable carcinogen (Jamshidi et al., 2020). Several government agencies consider PCE as a carcinogen (ATSDR, 2013). There is substantial evidence linking the causation of PCE to the health outcome of bladder cancer. (Minnesota Department of Health and Minnesota Poison Control System, 2018). We considered PCE for cancer risk assessment because the cancer slope factors for these substances are well established.

Air polluted with particulate matter, fumes (*i.e.*, volatile, or semi-volatile compounds), or aerosols can result in exposure through inhalation. Information on the levels of pollutants detected in the air and the duration of exposure is required to evaluate exposure through inhalation. The mean daily probable dose from the inhalation of contaminated air was determined using the following formula (USEPA, 2022, 2017):

$$ADD = \frac{(C_{air} \times IR \times ET \times EF \times ED)}{(BW \times AT)} \quad (2)$$

Where,

ADD = average daily dose (mg kg^{-1} day^{-1}),
C_{air} = the concentration of pollutants in the air (mg m^{-3}),
IR = inhalation rate (m^3 $hour^{-1}$),
ET = exposure time (hours day^{-1}),
EF = exposure frequency (days $year^{-1}$),
ED = exposure duration (years),
BW = body weight (kg), and
AT = average lifespan for carcinogens (70 years × 365 days/year), for non-carcinogens (30 years × 365 days/year).

Once a person has been exposed to a chemical for their entire life, the slope factor and the average daily dose are multiplied to determine the risk of cancer development (USEPA, 2004).

$$R_{air} = ADD \times CSF_i \quad (3)$$

where R_{air} is the cancer risk from breathing in contaminated air, and CSF_i is the inhalation cancer slope factor of the contaminant.

A widely used measure for assessing non-carcinogenic health risks is the hazard index (HI), which is calculated using Equation (4) (Lu et al., 2020):

$$HI = ADD / RFC \quad (4)$$

where HI represents the overall non-carcinogenic risk associated with exposure to a specific threshold pollutant. RFC is the non-carcinogenic reference concentration for toxic pollutants, expressed in mg/m^3. It is important to note that HI should be calculated separately for each pollutant. The measures of the variables that matched the Korean scenarios are presented in Table 1. To determine the non-carcinogenic risk associated with diverse pollutant sources, the HI value was calculated as the sum of the hazard index values for each pollutant present in the emission source. A higher HI value indicates a higher concentration of hazardous pollutants. The acceptability of the pollutant risk can be determined by comparing the calculated HI value with a threshold value of 1: When the HI value was <1, the level of pollutant risk was considered acceptable. However, HI values of 1 or greater indicate that the risk associated with pollutants is hazardous (McKenzie et al., 2012). Ambiguity in risk estimation can often lead to errors, particularly when uncertainty stems from a diverse range of human behaviors and characteristics. (Tarafdar and Sinha, 2022). A sensitivity analysis was performed using Spearman rank order correlations to determine which probability density functions had the greatest impact on risk estimation. Oracle's Crystal Ball (11.1.2.4.600) software was used for risk evaluation and sensitivity analysis (Tarafdar et al., 2020). The program generated a 95 percent confidence dimension for risk evaluation. To ensure numerical stability, an overall iteration count of 50,000 was used (Tarafdar and Sinha, 2018a, b). Additionally, Crystal Ball calculates the rank connection coefficients between each assumption and forecast while the simulation runs. The correlation coefficients indicate a substantial share of the number of assumptions and predictions that vary collectively.

Table 1
Exposure parameters and their range of variable values in probabilistic exposure risk assessments.

Definition	Units	Distributions	Adults	Data source
IR	m^3 hr^{-1}		0.833	(USEPA, 2015)
ED	year	Uniform	U (0, 42)	Verbal interrogation of authorities
BW	kg	Log-normal	LN (64.82, 1.18)	Korean National Health Insurance Corporation (NHIS, 2020)
EF	d $year^{-1}$	Log-normal	LN (252, 1.01)	(Chen and Liao, 2006; Nguyen et al., 2020)
ET	hr		8	Verbal interrogation of authorities
AT	day		70 × 365 for cancer 30 × 365 for non-cancer	Tarafdar and Sinha (2022) Lee et al. (2006)

LN (gm, gsd): geometric mean and standard deviation. U (min, max): minimum and maximum values.

3. Results and discussion

3.1. The distribution of VOCs in contaminated site

As shown in Table 2, the soil gas of the target VOCs in the park was lower than that in the contaminated site or was undetected, implying that the soil gas at the contaminated site was polluted with VOCs. The concentration of PCE in soil pores varied significantly, ranging from 12 to 5,400 μg m^{-3}. The concentrations of PCE in soil gas close to monitoring wells F and G were approximately 1–2 orders of magnitude higher than those close to the other monitoring wells. Monitoring wells F and G were close to each other, within 100 m, whereas other monitoring wells were more than 200 m away from monitoring well F. The results showed that groundwater close to monitoring well F acted as a source of PCE at the contaminated site. This was in line with the measurement of the PCE in the groundwater, as shown in Table S2. The PCE of the groundwater of monitoring well F was the highest. However, XYL and TOL were not detected in the groundwater at any monitoring wells. The XYL and TOL concentrations in the soil gas at the contaminated sites were not significantly different depending on sampling sites. The distributions of TOL and XYL in the contaminated site appeared to be different from that of PCE. Plant emissions at contaminated sites could be a source of XYL

Table 2
VOCs concentrations (μg m^{-3}) of soil vapor. Values in the parentheses mean standard deviations (n = 3).

Site	A	B	C	D	E	F 1	F 2	F 3	G 1	G 2	Park
TOL (LOD: 10)	110 (±22)	92 (±15)	45 (±24)	64 (±26)	46 (±7.6)	100 (±23)	130 (±41)	260 (±190)	81 (±6.2)	86 (±6.2)	15 (±1.7)
PCE (LOD: 6.2)	30 (±17)	15 (±0.56)	16 (±0.49)	13 (±1.6)	12 (±0.97)	5,400 (±910)	5,200 (±990)	1,700 (±360)	500 (±260)	490 (±56)	–
XYL (LOD: 2.4)	14 (±7.8)	7.6 (±0.88)	3.6 (±0.86)	4.1 (±0.96)	3.3 (±0.036)	7.6 (±0.93)	7.1 (±0.92)	10 (±3.4)	10 (±2.0)	6.4 (±0.10)	–

[a]Limit of detection (μg m^{-3}).

and TOL.

Generally, the concentrations of VOCs in the air 0 m and 1 m above the soil surface were not significantly different, as shown in Table 3. A height of 1 m may need to be increased to observe the diffusion of VOCs in the air because of the good mixing conditions of the air. Another reason could be using a pump that mixes air for active sampling. As an exception, the concentrations of TOL and XYL in the air 1 m above the soil near monitoring well F were significantly higher than the corresponding values in the air 0 m above the ground. VOC concentrations in the air 0 m and 1 m above the park soils were lower than those at the contaminated site or undetected. In contrast to the variation observed in soil pores, the concentration of PCE in the air showed negligible variations, ranging from 0.45 to 1.5 μg m^{-3}. Concentrations of TOL in the air at 0 m and 1 m above soils near monitoring well C were approximately one order of magnitude higher than those at the other sites. The air pollution near C, such as industrial stack emissions was estimated to be the source of the TOL.

Fugacity refers to the tendency of a chemical to escape from belonging media (Mackay, 2004). The fugacity of VOCs in air and soil vapor was compared to estimate their fate in the soil (Meijer et al., 2003; Wang et al., 2011). The fugacity fraction (f_f) is an easy and conventional method for determining whether phases are in equilibrium.

$$f_f = f_S / (f_S + f_G) \tag{5}$$

where the fugacity of VOCs in the soil is f_S the fugacity of VOCs in the air is f_G. In this study, the VOCs concentrations in the soil and soil vapor were at equilibrium. Therefore, the fugacity of VOCs in soil was equal to that in soil vapor, which is given by:

$$f_s = 10^{-12} C_g RT / M_W \tag{6}$$

where, R is the universal gas constant (8.314 Pa m^3 K^{-1} mol^{-1}), T is the temperature (K), and MW is the molecular weight (g mol^{-1}). When C_{air} is the concentrations of VOCs in outdoor air (μg m^{-3}), f_G is given by:

$$f_s = 10^{-12} C_{air} RT / M_W \tag{7}$$

When the fugacity fraction was more significant than 0.7, the soil acted as a source, and VOCs volatilized from the soil to the air. When the fugacity fraction is lower than 0.3, the soil appears to act as a sink (Harner et al., 2006; Pham et al., 2022), and VOCs are deposited from the air to the soil. The fugacity fractions of the VOCs were calculated using the VOC concentrations in the soil vapor and air, as shown in Table S3. The fugacity fractions of VOCs of air 0 m above soils and soils were shown in Fig. 2. Emissions from plants near soil close to monitoring well C could be a source of TOL because of the much lower fugacity fractions. The soil close to monitoring wells F and G, where groundwater concentrations of PCE were relatively high, appeared to act as a source of PCE because the fugacity fractions were greater than 0.97. However, the fugacity fractions in the soil close to monitoring wells A-E, where groundwater concentrations of PCE were relatively low, were 0.37–0.50. Fugacity calculations indicated that the PCE at the test site originated from groundwater. Plant emissions at contaminated sites could be a source of XYL because all the calculated fugacity fractions were lower than 0.3.

The vapor intrusion attenuation factors empirically derived by the USEPA were used to estimate the indoor air concentrations of VOCs (EPA, 2015; Guidance for Supplementary Vapor Intrusion, 2020). For soil gas, 0.03 is the recommended attenuation factor. The indoor air concentrations of VOCs by vapor intrusion were estimated using the measured VOC concentrations of the soil gas, as shown in Table S4. Generally, groundwater concentrations are not recommended for evaluating vapor intrusion because of uncertainties related to partitioning and transport. When the measurement of soil gas is unavailable, the groundwater concentration can be used to evaluate vapor intrusion. In this case, Henry's law constants predicted the equilibrium vapor concentrations. The PCE concentrations of the vapor at equilibrium with the groundwater were predicted, as shown in Table 4. To estimate the vapor intrusion from groundwater to indoor air, the USEPA recommends an attenuation factor of 0.001. As shown in Fig. 3, for the sampling site close to the estimated source, monitoring well F, the ratio of groundwater to soil gas was close to 30. For example, groundwater-to-soil gas ratios were 28, 29, 90, 14, and 14 for sampling sites F1, F2, F3, G1, and G2, respectively. However, the groundwater-to-soil gas ratio increased when the sampling site was far from the source. The groundwater-to-soil gas ratios were 2400, 500, 630, 670, and 560 for sampling sites A, B, C, D, and E, respectively. The result indicates that passive sampling of gaseous VOCs in soil pores would be helpful for accurate risk assessment. Although the R^2 value for the regression analysis between fugacity fractions and groundwater-to-soil gas ratios was 0.53, the analysis was statistically significant with *F*-value (0.017) lower than 0.05. The *p*-values of the fugacity fractions and the intercept were 0.017 and 0.0047, respectively. The groundwater-to-soil gas ratios (R) can be estimated as

$$R = 1800(1 - f_f) \tag{8}$$

The results also suggest that the lateral diffusion from the source, rather than the source's concentration, determines the vapor intrusion level. This is in line with previous studies showing that lateral diffusive transport is a crucial factor in determining the extent of the influence area of a contamination plume on soil vapor intrusion, which is a significant pathway for exposure to VOCs at contaminated sites as it leads to the attenuation of soil gas concentrations (Wang et al., 2020). A buffer zone of 30 m in both the vertical and lateral directions from the contaminant source was recommended (USEPA, 2002) based on the findings of a theoretical study that indicated that vapor intrusion impacts were not observed beyond one or two houses from the estimated edge of the groundwater plume (Lowell and Eklund, 2004; Folkes et al., 2010). Numerical simulations conducted by Abreu and Johnson (2005) also demonstrated that when the vapor source is located 20 m away from the building and 8 m beneath the ground surface, the concentration attenuation factors from the source to the indoor air can be approximately two orders of magnitude lower than when the vapor source is located beneath the building foundation. Field conditions, such as the heterogeneity of the soil and pavement, can also affect the attenuation of soil gas concentrations (Wang et al., 2019). As most of the area in the contaminated site selected in this study was blocked by pavement, the surface pavement could intensify VOCs in the surface soil vapor.

Table 3
VOCs concentrations (μg m^{-3}) of air 0 m and 1 m above soils.

Site	A		B		C		D		E		F1		F2		F3		G		Park	
Height	0 m	1 m	0 m	1 m	0 m	1 m	0 m	1 m	0 m	1 m	0 m	1 m	0 m	1 m	0 m	1 m	0 m	1 m	0 m	1 m
TOL (LOD: 0.16)	3.5	2.9	2.7	3.1	74	40	2.3	2.4	3.1	2.5	2.7	9.9	3.3	2.8	5.5	3.1	3.1	3.2	2.1	2.0
PCE (LOD: 0.14)	1.5	1.3	0.54	0.58	0.48	0.51	0.50	0.45	0.46	0.54	0.78	0.59	0.58	0.60	0.58	0.61	0.52	0.51	–	–
XYL (LOD: 0.12)	1.7	1.9	1.2	1.5	7.5	3.6	0.81	0.65	1.2	0.99	0.95	5.7	1.2	1.2	1.3	1.9	0.95	1.2	0.49	0.45

[a]Limit of detection (μg m^{-3}).

3.2. Risk assessment

The inhalation cancer risks from the PCE and HI values of TOL and XYL were assessed for street cleaners. We conducted an interview with the authorities at Iksan City Hall to gather information about street cleaners. According to them, the cleaners cover 7 km every day, which is shorter than the length of roads in contaminated areas. Based on this information, we can assume that the street cleaners are exposed to contamination throughout their working hours. Average body weights for Korean men and women were 72.7 kg and 57.8 kg, respectively (NHIS, 2020). The geometric mean and standard deviation of the body weights of both genders (64.82, 1.18) were used for risk assessment. We used the outdoor air concentrations of TOL, XYL, and PCE at polluted locations 1 m above the ground and at ground level. The cancer slope factor for the PCE (0.021) provided by the OEHHA (2011) was used. RFC reference values of toluene (5 mg m^{-3}) and 0.1 mg m^{-3} for xylene were used (McKenzie et al., 2012). The results are shown in Fig. S3. As shown in Fig. 4, the 95% cancer risk for PCE was in the range of 10^{-6} to 10^{-4}, indicating a low plausible hazard (NYS, 2012). However, ATDSR (2022) states that at this level of risk, public education on exposure reduction strategies or ongoing monitoring can be considered, particularly if the pollutant can migrate and people can be exposed to greater levels. The 95% HI values of TOL and XYL were in 10^{-1} to 10^{-3}, which were less than 1, indicating that the risks of TOL and XYL were considered acceptable. According to the measured concentrations of outdoor air at ground level and 1 m above the ground, there were no noticeable differences in the risks of air at these two elevations.

The input parameters were rated based on their impact on output risk in a quantitative sensitivity analysis and presented as tornado plots. Using this information, we can focus on the factors that impact the simulation outcomes most. The sensitivity analysis results of the cancer risk simulation were displayed as tornado plots with Spearman rank-order correlation coefficients expressed as percentages. The contributions of exposure duration were the highest for XYL (59–61%) and PCE (78–84%). Exposure duration (ED) was followed by contributions from air concentrations of VOCs, except TOL, where the concentration in air was the main contributor (51–58%). The sensitivity analysis suggests that to increase the accuracy of risk assessment, efforts should be made to define the probability distribution for the parameter of exposure durations (ED) more precisely. The outdoor air concentrations above the contaminated sites were higher than those above the park. The risk of inhalation cancer may be significant at contaminated sites.

For the inhalation cancer and non-cancer risk assessments for vapor intrusion, the estimated indoor air concentrations shown in Table S4 were used. Inhalation cancer and non-cancer risks were assessed for office workers in a building near monitoring wells F and G. We used the estimated indoor air concentrations at F1, F2, F3, G1, and G2, which were close to the target building within a 50 m radius. The results are shown in Fig. S4. As shown in Fig. 4, the 95% inhalation cancer risk for the vapor intrusion of the PCE was higher than that for outdoors. The cancer risk associated with PCE increased by more than 100 times. The cancer risk for vapor intrusion of PCE was in the range of 10^{-3}~10^{-2}, indicating a high risk (NYS, 2012). Research on potential methods to reduce (as much as feasible) the public's exposure to environmental carcinogens should be conducted. Community healthcare providers and the public should be informed about potential ways to reduce their exposure. The 95% HI values of TOL and XYL were in 10^{-2} to 10^{-4}, which were much less than 1, indicating that the risks of TOL and XYL were considered acceptable. The contribution of air concentration was the highest for PCE (62%). The duration of exposure to TOL and XYL was the highest. Direct measurement of indoor air in buildings would be more appropriate for risk assessment and could be a future endeavor. In the case of screening vapor intrusion risk assessments for buildings, profiling the diffusion of VOCs from the source would be helpful.

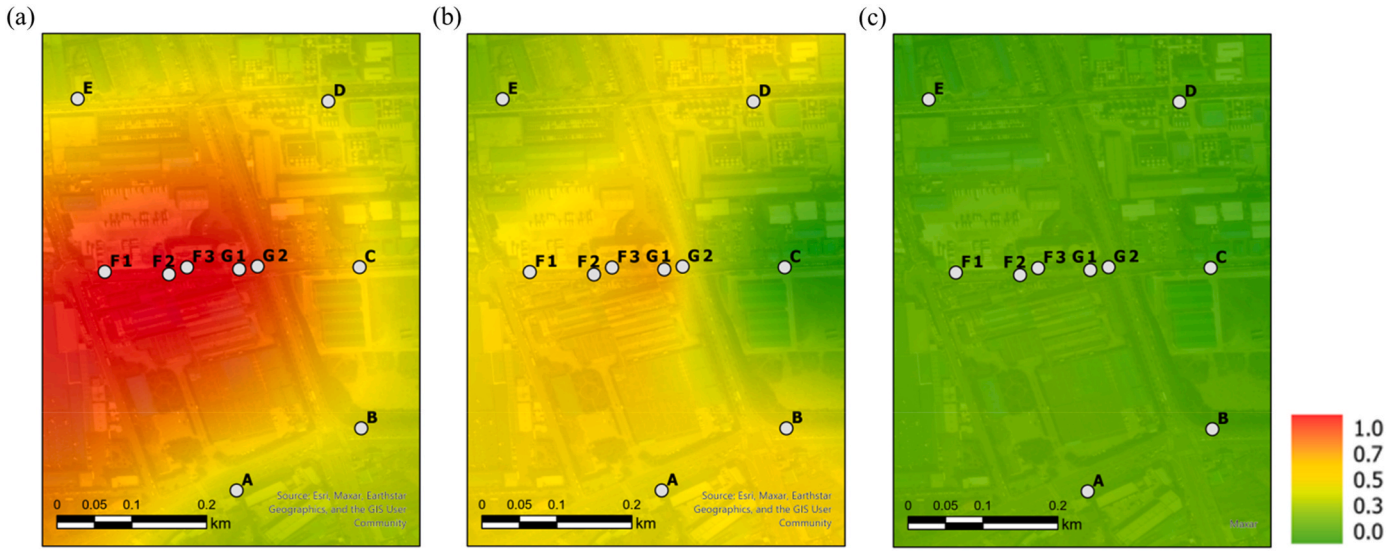

Fig. 2. The spatial distribution of fugacity fractions (fugacity in surficial soil gas devided by fugacity in air) of (a) PCE, (b) TOL, and (c) XYL. Note that when the fugacity fraction is greater than 0.7 which is shown as red color, the soil becomes the source of VOCs.

Table 4
Diffusion of PCE from ground water through soil to air. Values in the parentheses mean standard deviations (n = 3).

Site	A	B	C	D	E	F 1	F 2	F 3	G 1	G 2
Air 1 m above soil (μg m^{-3})	1.3	0.58	0.51	0.45	0.54	0.59	0.60	0.61	0.51	0.51
Air 0 m above soil (μg m^{-3})	1.5	0.54	0.48	0.50	0.46	0.78	0.58	0.58	0.52	0.52
Estimated indoor air (μg m^{-3})	0.89 (±0.051)	0.46 (±0.0017)	0.49 (±0.0015)	0.40 (±0.0048)	0.36 (±0.0029)	160 (±2.7)	150 (±3.0)	50 (±1.1)	15 (±0.78)	15 (±0.17)
Soil vapor (μg m^{-3})	30 (±17)	15 (±0.56)	16 (±0.49)	13 (±1.6)	12 (±0.97)	5,400 (±910)	5,200 (±990)	1,700 (±360)	500 (±260)	490 (±56)
Predicted vapor from ground water (μg m^{-3})[a]	70,000	7,500	10,000	8,900	6,800	150,000	150,000	150,000	6,800	6,800
Ground water/Soil vapor	2,400 (±1,300)	500 (±19)	630 (±19)	670 (±75)	560 (±45)	28 (±3.4)	29 (±5.9)	90 (±24)	14 (±6.5)	14 (±1.7)

[a] Henry's law constant (at 298 K) in Table S1 was used to calculate concentration of vapor from ground water.

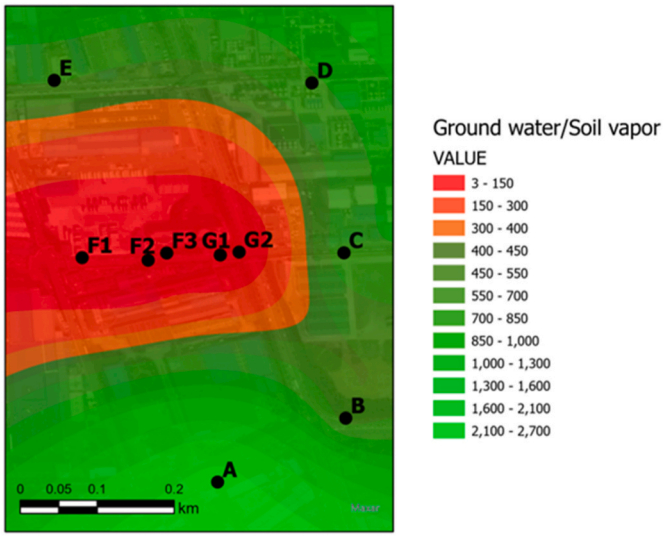

Fig. 3. The spatial distribution of PCE attenuation factor (gaseous PCE concentrations calculated from Henry's Law constant and groundwater PCE concentrations divided by PCE concentrations in surficial soil measured by passive sampler).

4. Conclusions

This study examined the distribution of VOCs at contaminated sites. The results of this study demonstrate that passive sampling offers a significantly less costly and labor-intensive approach compared to traditional methods for assessing contaminant distribution at contaminated sites and characterizing risk. This highlights the potential for wider application of passive sampling techniques in environmental studies. The fugacity fraction, calculated by passive soil vapor sampling and active air sampling, can be used to predict the source and fate of VOCs in contaminated sites. The results highlight the critical importance of conducting a vapor intrusion risk assessment using passive sampler measurements of gaseous VOCs in soil pores. This approach is essential for accurate risk characterization and assessment. Lateral diffusion from the source was found to be more important than source concentration or vertical diffusion from the source. This suggests that lateral movement of VOCs should be considered in risk assessment. To further understand the distribution of VOCs in contaminated sites, soil gas sampling at each depth and direct measurement of indoor air inside buildings at contaminated sites are required.

Credit author statement

Pil-Gon Kim: Conceptualization, Investigation, Writing – original draft. Abhrajyoti Tarafdar: Data curation, Writing – review & editing.

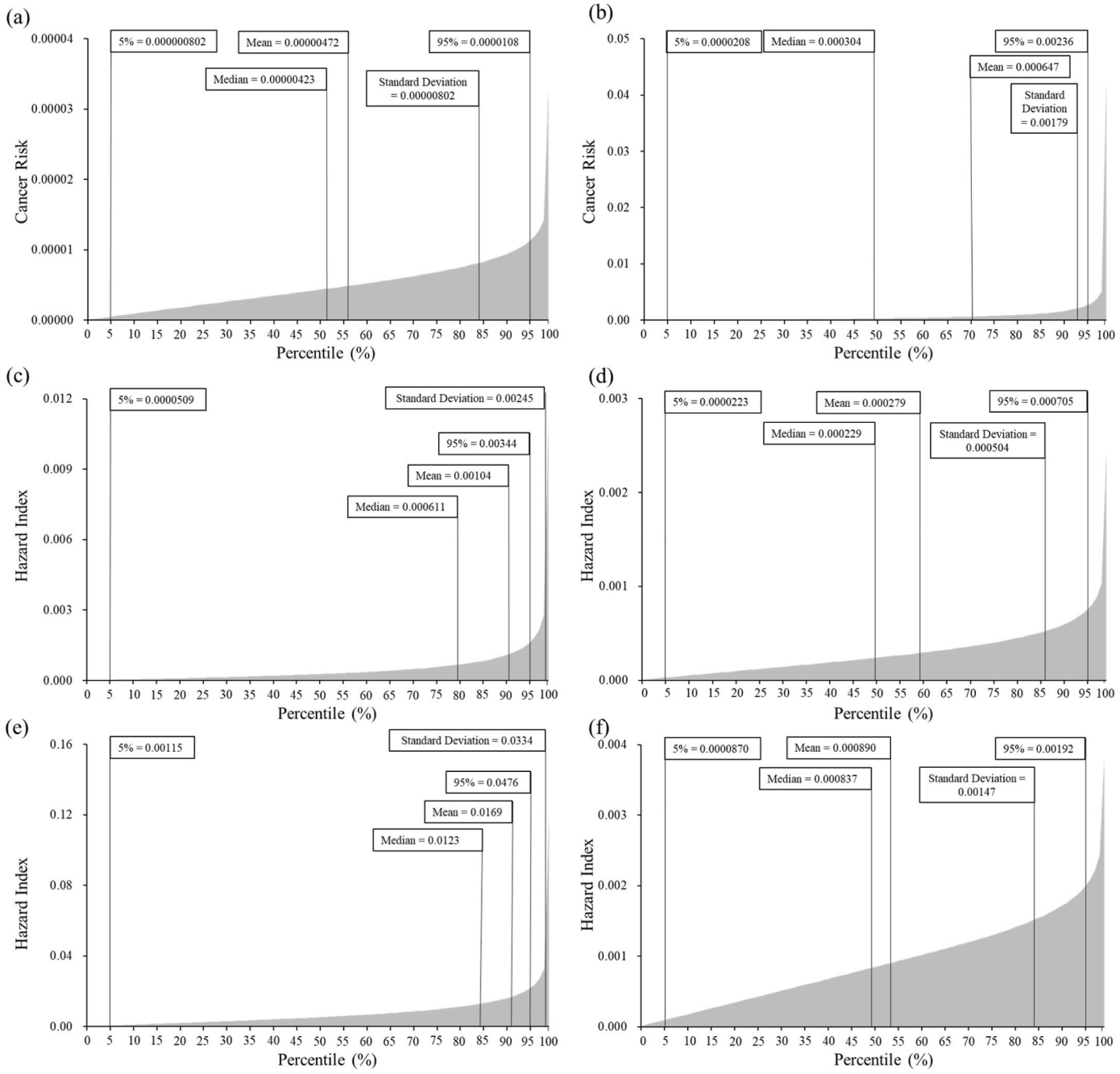

Fig. 4. Estimated cancer risks of PCE and HI values of TOL and XYL for outdoor air 1 m above soil (a), (c), (e) and vapor intrusion (b), (d), (f).

Keum Young Lee: Data curation, Investigation. Jung-Hwan Kwon: Conceptualization, Writing – review & editing. Yongseok Hong: Conceptualization, Funding acquisition, Supervision, 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.envres.2023.117238.

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