



Appropriate control measure design by rapidly identifying risk areas of volatile organic compounds during the remediation excavation at an organic contaminated site

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Abstract Many organic contaminated sites require on-site remediation; excavation remediation processes can release many volatile organic compounds (VOCs) which are key atmospheric pollutants. It is therefore important to rapidly identify VOCs during excavation and map their risk areas for human health protection. In this study, we developed a rapid analysis and assessment method, aiming to and reveal the real-time distribution of VOCs, evaluate their human health risks by quantitative models, and design appropriate control measures. Through on-site diagonal distribution sampling and analysis, VOCs concentration showed a decreasing trend within 5 m from the excavation point and then increased after 5 m with the increase

in distance from the excavation point ($p < 0.05$). The concentrations of VOCs near the dominant wind direction were higher than the concentrations of surrounding pollutants. In contrast with conventional solid-phase adsorption (SPA) and thermal desorption gas chromatography–mass spectrometry (TD-GC/MS) methods for determining the composition and concentration of VOCs, the rapid measurement of VOCs by photo-ionization detector (PID) fitted well with the chemical analysis and modeling assessment of cancer/non-cancer risk. The targeting area was assessed as mild-risk (PID < 10 ppm), moderate-risk (PID from 10 to 40 ppm), and heavy-risk (PID > 40 ppm) areas. Similarly, the human health risks also decreased gradually with the distance from the excavation point, with the main risk area located in the dominant wind direction. The results of rapid PID assessment were comparable to conventional risk evaluation, demonstrating its feasibility in rapidly identifying VOCs releases and assessing the human health risks. This study also suggested appropriate control measures that are important guidance for personal protection during the remediation excavation process.

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Introduction

With the rapid development of chemical engineering, more organic contaminants were found at industrial sites, causing serious environmental problems and concerns (Kermani et al., 2021). During in situ remediation of organic contaminated sites, volatile organic compounds (VOCs) emitted from excavation can cause risks to human health, and considerable studies have been conducted to describe the risks of VOCs to human health (Kermani et al., 2021; Kumar et al., 2021; Wu et al., 2021). Once excavated or disturbed, the concentrated VOCs might volatilize in a short period, causing increased atmospheric contamination and environmental/health risks (Ma et al., 2016). VOCs are rapidly dispersing and highly toxic, requiring practical techniques for the fast identification and evaluation of the regional risks at/around the construction areas (Masih et al., 2021; Zhang et al., 2020). Therefore, there is a necessity to establish a rapid identification method of human health risks from VOCs at contaminated sites to protect workers exposed to contaminated air or during remediation excavation of organic contaminated sites.

Many analytical methods and models have been investigated to address risk assessment of contaminated sites (Ma et al., 2016; Zhang et al., 2020). Wang et al. applied an activated carbon–silica gel sampler to extract VOCs for the optimization of indoor work environment assessment (Wang et al., 2021). The CARO-PLUS model was developed to computationally evaluate the human health risk at the organic contaminated sites, and the lifetime cancer risk (LCR) was introduced to assess the mean exposure of target human groups based on the carcinogenic potency of specific toxic compounds (de Oliveira Galvao et al., 2018). The human health risk data were important for assessing the possible and alternative protection methods during the site excavation process (Sazakli & Leotsinidis 2020). Although these models were accurate for VOCs toxicity assessment, they all rely on complex sampling and expensive chemical analysis such as solid-phase adsorption (SPA), headspace gas chromatography with flame ionization detection (GC-FID), and thermal desorption gas chromatography–mass spectrometry (TD-GC/MS) (Bulatovic et al., 2022; Liu et al., 2022; Zheng et al., 2020). Therefore, the time-consuming data interpretation and model forecasting for human health risks brought

the challenge of meeting the practical requirements for rapid risk assessment. It is important to investigate fast analytics and assessment for the human health risks at the excavation sites.

In this study, we developed a fast and real-time analytical/assessment method to evaluate the human health risks at an excavation site in Beijing, China. We aimed to: 1) collect atmospheric samples and compare results from SPA TD-GC/MS and photoionization detector (PID), 2) quantify the contamination level and human health risks by visualizing various risk level at/around the remediation excavation site, and 3) suggest appropriate control measures for personal protection during the remediation process.

Materials and methods

Sampling site

The study was conducted at a chemical plant in Beijing, China (north latitude 39°53'11'' and east longitude 116°29'27'), which was abandoned in 2005. The permissions for the sampling activities were authorized by Beijing Environment Agency who was applying the remediation excavation process, and the field studies did not involve endangered or protected species. The main products of the chemical plant included polyvinyl chloride resin, sodium hydroxide, hydrochloric acid, chloride, calcium carbide, and phthalic anhydride. The air sampling was conducted in July 2013, during the site remediation excavation process, and the sampling facilities were portable meteorological instruments Kestrel 4500 and portable anemometers PH-1A. During the sampling process, the measured wind speed was 1.1 m/s with the north-east wind direction. The air pressure was 102 kPa measured by DYM3 aneroid barometer.

According to the preliminary monitoring results at the contaminated site, the main VOCs pollutants included benzene/toluene/ethylbenzene/xylene (BTEX), organochlorine solvents, organochlorine pesticides, persistent organic pollutants (POPs), polycyclic aromatic hydrocarbons (PAHs), and dioxins, all of which are typical atmospheric pollutants at the organic contaminated sites (Davidson et al., 2021). This research addressed the monitoring and risk assessment of 1, 2-dichloroethane, chloroform, carbon tetrachloride, and 1, 1, 2-trichloroethane, which

were the dominant pollutants at the site due to the actual production profiles.

Sample collection

Air sample collection followed an amendment linear distribution method as illustrated in Fig. 1 (Liao et al., 2003). According to the site topography and other field conditions, the 45° in the sector sampling method was adjusted to 30°, while the sampling points on each sampling line were arranged to be dense first and then sparse. Along the dominant wind direction, a sampling line is set up, and two sampling lines are set up on both sides of the main line at 30° direction, respectively. In the main sampling line, the distance from the pollution source is 1, 3, 5, 10, 15, 20, and 25 m. The distance of each sampling line on both sides of the main sampling line is 1, 3, 5, 10, 15, and 20 m. Among them, the background samples were collected in the upwind direction of the soil excavation point, marked as No.1 and No.2, respectively. The sampling points on the sampling line from near to far are No.3, No.4, No.5, No.6, No.7, and No.8, the sampling points on the sampling line in the dominant wind direction are marked as No.9, No.10, No.11, No.12, No.13, No.14, and No.15, the sampling points on the sampling line above are marked as No.16, No.17, No.18, No.19, No.20, and No.21. The closest sampling point to the excavation point is marked as No.22, as suggested by previous research (Collins et al., 2014).

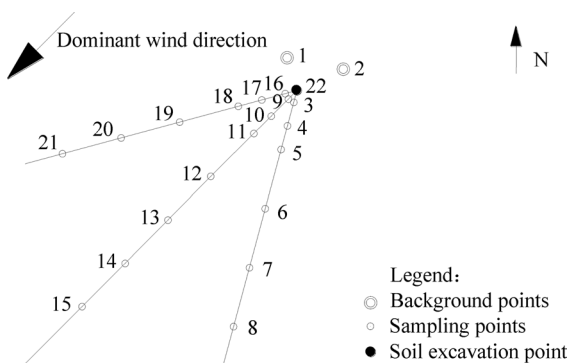


Fig. 1 Location of excavation and sampling points. The sampling points (No. 3 to No. 21) were located at 1, 3, 5, 10, 15, 20 and 25 m from the excavation point (No. 22). The background samples were located in the upwind direction (No. 1 and No. 2). Arrow refers to the dominant wind direction

The sampling was conducted on a sunny day, and no rainfall occurred for 3 days before the experiment. During the sampling process, only one excavator (PC240LC-8M0, KOMATSU, Japan) was operated in a small area, which was viewed as a point excavation. The atmospheric sample collection was conducted by Czmero tube Sampler filled by CarbopackC/CarbopackB/CarbosieveS at 0.10 L/min flow rate. The sampling process lasted for 20 min as suggested (Xu et al., 2021a) and the sampler height was set as 1.5 m from the ground, which was human respiratory similar position for better evaluating the impacts of VOCs on human health (Nie et al., 2018). The atmospheric samples were stored in aluminum plastic composite film sampling bags, sealed, refrigerated, and transported to laboratory. The PID data were obtained within the same period of time by moving the PID equipment from point to point at the height of 1.5 m. Since PID detects the total amount of VOCs, it can effectively reflect the integral dispersion trend of VOCs. Three individual replicates were carried out for each sampling point. Background points were collected when the contaminated site was not disturbed by excavators following the same procedures described above, as a comparison of background values of pollutant concentrations in air.

Analytical methods

The composition and concentration of 9 VOCs were measured using a solid-phase adsorption (SPA) and thermal desorption gas chromatography–mass spectrometry (TD-GC/MS) method (Atlan et al., 2006). The analysis was conducted by Shimadzu GC–MS 2021 plus with DB-VRX chromatographic column (60 m×0.32 mm×1.8 μm). Nitrogen was the carrier gas and the flow rate was 60 ml/min. After desorption for 10 min at 280 °C, the sample was injected with high-purity helium (99.999%) and the flow rate was 1.0 ml/min. The initial temperature was kept at 30 °C for 2 min, followed by heating to 200 °C at the rate of 8 °C/min. With 70 eV electron ionization energy, the mass range was from 35 to 300 amu. Each peak was scanned at least 20 times and each scanning did not exceed 1 s. The method detection limit (MDL) was 0.001 ppm, and the method linear detection range (MLDR) was 0.001 ppm to 100 ppm. To ensure the accuracy of results, quality assurance (QA) and quality control (QC) procedures were implemented for

all samples. Besides background air samples (No.1 and No.2 collected in the upwind direction of the soil excavation point), blank samples (Czmero tube without connection to sampler) were also prepared as blank control.

Bromochloromethane was used as the surrogate standard to calculate the recoveries of VOCs in different samples, which ranged from 91.4% to 118.5%.

Photo-ionization detector (PID, PGM-7340, RAE Systems, USA) was utilized for fast detection of the atmospheric concentration of total VOCs (TVOCs). The analytical PID measurement included saturated/unsaturated hydrocarbons, aromatic hydrocarbons, aldehydes, ketones, ethers, and halogenated hydrocarbons (Davardoost & Kahforoushan 2018). It is an effective tool for rapid monitoring of TVOCs to evaluate the real-time air pollution distribution in/around remediation area, thereby for fast assessment of VOCs risks. Before the field sampling and measurement, the PID was calibrated by nitrogen/oxygen (80/20, v/v) gas as negative control and 100 ppm isobutylene gas as standard. The calibration process followed the flow rate of 0.3 L/min with a probe calibration cap, in accordance with manufacturer's instructions. The MDL was 0.001 ppm and the MLDR was 0.001 ppm to 10,000 ppm.

The contour graphs of PID data, cancer risk, and non-cancer risk at the site were plotted by OriginPro 8.0, from the original data and risk calculation from the models.

Human health risk assessment

During the remediation excavation at organic contaminated site, the main VOCs exposure pathway is inhalation which damages people's health ultimately (Zhao et al., 2020). There are many factors that affect respiratory exposure, such as environmental VOC concentration, exposure time, human age and gender, respiratory level influenced by exercise status, etc. Therefore, the respiratory exposure should be reasonably calculated. The quantification of the VOCs inhalation follows Eq. (1) as (Davison et al., 2008):

$$ADD = \frac{C \times IR \times ET \times EF \times ED}{BW \times AT} \quad (1)$$

where ADD (absorbed dose) refers to VOC's daily respiratory exposure dose (mg/kg/d). C represents VOCs concentration in ambient air (mg/m^3), and IR is the respiratory rate (m^3/d), valued $20 \text{ m}^3/\text{d}$ in this research as suggested by US Environmental Protection Agency (U.S. EPA). ET refers to the exposure time for each event (h/time) with the value of 5 h/d here, whereas EF is the exposure frequency (d/a). ED , BW , and AT represent the duration of exposure (a), body mass (kg), and the average exposure time (d), respectively.

Non-cancer risks in a single contaminant exposure pathway are quantified by the ratio of the average unit weight of entire average daily inhalation (CDI) to the chronic reference dose (RfD) (Jansen et al., 2009a, 2009b), expressed as the hazard quotient (HQ) in Eq. (2). The joint non-carcinogenic risk is used to express the total risk values in the presence of multiple contaminants with multiple possible exposure routes which is expressed by hazard index (HI) in Eq. (3).

$$HQ = \frac{CDI}{RfD} \quad (2)$$

$$HI = \sum_{j=1}^{n_1} \sum_{i=1}^{n_2} \frac{CDI_{ij}}{RfD_{ij}} \quad (3)$$

Here, CDI_{ij} is the average daily unit exposure dose of i th type contaminant on the j th type exposure pathway, and RfD_{ij} is chronic reference dose of i th type contaminant on the j th type exposure pathway, as listed in Supporting Information Table S1 (USEPA, 2004). n_1 and n_2 refer to the number of non-cancer risk pollutants and exposure pathways, respectively.

For contaminant exposure pathway, the cancer risks (R) of an individual contaminant and the joint cancer health risks (R_j) of multi-contaminants follow the expression of Eq. (4) and (5). When VOCs concentration is higher than >0.01 ppm, as the VOCs contamination level in this study, the impulse model is suitable to predict the modified joint cancer health risks (R_j'), as listed in Eq. (6) (Seco et al., 2007):

$$R = CDI \times SF \quad (4)$$

$$R_I = \sum_{j=1}^{n_1} \sum_{i=1}^{n_2} CDI_{ij} \times SF_{ij} \tag{5}$$

$$R'_I = \sum_{j=1}^{n_1} \sum_{i=1}^{n_2} [1 - \exp(-CDI_{ij} \times SF_{ij})] \tag{6}$$

Here, $SF_{i,j}$ is the cancer slope factor (Table S1) of i th type contaminant on the j th type exposure pathway (USEPA, 2004). n_1 and n_2 represent the number of cancer risk pollutants and exposure pathways, respectively. In this study, inhalation exposure pathway model is the key tool to determine joint health risks of VOCs during site remediation process.

Results and Discussion

Pollutant distribution

VOCs analysis results of SPA followed by TD-GC/MS indicated that the major atmospheric contaminants included 1,1-dichloroethylene (ranging from 0.051 ppm to 0.558 ppm, 3.81 to 41.64 times higher than background, respectively), chloroform (0.32 ppm to 4.51 ppm, 3.87 to 54.57 times higher than background, points No. 1 and No. 2), carbon tetrachloride (0.43 ppm to 6.34 ppm, 31.50 to 464.47 times higher than background), trichloroethylene (0.019 ppm to 0.169 ppm, 3.49 to 31.01 times higher than background), 1, 1-dichloroethane (0.15 ppm to 2.55 ppm, 3.35 to 56.92 times higher than background), and 1, 1, 2-trichloroethane (0.15 ppm to 1.24 ppm, 3.11 to 25.70 times higher than background), as listed in Table 4. There were some other contaminants such as 1, 2-dichloroethane, benzene, and tetrachlorethylene, the contamination level of which was 0.58–3.19, 1.35–3.46, and 1.98–12.89 times of background (Points No. 1 and No. 2). It is noteworthy that VOCs concentrations showed a rapid decrease and then an increase within 5 m from the excavation point, which might be attributing to the excavation which was intermittent rather than continuous, and VOCs were produced as discontinuous gas clouds. After 5 m from the excavation point, the VOCs concentration gradually decreased with the increase in distance ($p < 0.05$).

Generally, VOC contamination decreased with the distance to the excavation point, similar to previous

research (Zhang et al., 2020). In particular, the spatial distribution of VOCs at contaminated sites was closely related to the layout and geological structure of the site, with surface soil more likely to contain large amounts of VOCs (Ye et al., 2023; Zheng et al., 2023). Given the atmospheric VOCs generation process, the intermittent gas plume was released by the discontinuous excavation activities and affected by the complex site topography. It has also been shown that soil disturbance due to the excavation process may also result in peak VOCs in the dominant wind direction (Wang et al., 2023). The atmospheric VOCs plume therefore was modeled with the puff model, and the integral of separate contamination plumes was done with Gaussian dispersion distribution (Karamchandani et al., 2020; Ou-Yang et al., 2020).

Assessment of human health risks

The field excavation activities consequently resulted in the atmospheric VOCs, showing the exceeding contamination and high health risk on the workers on-site (Cui et al., 2020). Based on Eq. (1) to (6) in Materials and Methods section, the distribution of human health risks at the site is calculated and illustrated in Table 1, Table 2, and Fig. 2. Both non-cancer and cancer risks gradually decreased with the increasing distance from the excavation point ($p < 0.05$). Using toxicity values of the US EPA Integrated Risk Information System (IRIS), significant human health risks were found at the contaminated sites during the remediation excavation process (Som et al., 2008). In the dominant wind direction, the cancer and non-cancer risks were above 0.10 and 40 at the points with 4–9 m distance to the excavation point, evaluated as the heavy-risk level. For the distance of 9–26 m away from the excavation point, the cancer risk was between 0.02 and 0.10, and the non-carcinogenic risk ranged from 10 to 40, indicating the moderate-risk region. Beyond 26 m away from the excavation point, the non-cancer and cancer risk was less than 10 and 0.02, respectively, classified as the region with mild risk.

The 1, 2-dichloroethane was identified as the key contaminants causing human health risks at this site, contributing to the majority of non-cancer risks (91.8–96.1%), followed by benzene (0.9–3.7%) and carbon tetrachloride (0.4–2.5%). The non-carcinogenic effects of benzene exposure include drowsiness,

Table 1 Non-cancer risk analysis at the study site. Data for individual VOCs are hazard quotient (HQ) as calculated in Eq. (2), and data for total non-cancer risk are hazard index (HI) as calculated in Eq. (3)

Distance to excavation point (m)	Sample	Non-cancer risks									
		1,1-dichloroethylene	1,2-dichloroethane	Chloroform	Benzene	Carbon tetra-chloride	Trichloroethylene	Tetrachloroethylene	1,1-dichloroethane	1,1,2-Trichloroethane	Total
1	No 3	0.1399	6.7253	0.0463	0.2636	0.0692	0.0413	0.0107	0.0259	0.0000	7.32
	No 9	0.0220	6.7253	0.0463	0.2636	0.0692	0.0413	0.0107	0.0259	0.0000	7.20
	No 16	0.2394	27.8075	0.5000	0.2767	0.5416	0.1971	0.0193	0.3684	0.1097	30.06
3	No 4	0.1356	27.1950	0.0597	0.3459	0.7321	0.2536	0.0262	0.4232	0.1381	29.31
	No 10	0.2334	27.1950	0.0597	0.3459	0.7321	0.2536	0.0262	0.4232	0.1381	29.41
	No 17	0.1322	30.0125	0.5788	0.4145	0.4370	0.2536	0.0222	0.4060	0.1195	32.38
5	No 5	0.1746	32.2175	0.6462	0.3431	0.5860	0.3116	0.0298	0.4369	0.1662	34.91
	No 11	0.1927	32.2175	0.6462	0.3431	0.5860	0.3116	0.0298	0.4369	0.1662	34.93
	No 18	0.1347	24.0100	0.4313	0.2713	0.3926	0.1661	0.0155	0.2844	0.0844	25.79
10	No 6	0.1270	32.4625	0.5889	0.4345	0.5387	0.3138	0.0314	0.3666	0.1777	35.04
	No 12	0.1128	32.4625	0.5889	0.4345	0.5387	0.3138	0.0314	0.3666	0.1777	35.03
	No 19	0.0609	16.7825	0.2407	0.2156	0.1848	0.0847	0.0091	0.1521	0.0440	17.77
15	No 7	0.0424	23.6425	0.3482	0.3974	0.4570	0.2235	0.0249	0.2107	0.1175	25.46
	No 13	0.0798	23.6425	0.3482	0.3974	0.4570	0.2235	0.0249	0.2107	0.1175	25.50
	No 20	0.0413	17.7625	0.2178	0.3088	0.1519	0.0853	0.0099	0.1294	0.0428	18.75
20	No 8	0.0845	18.4975	0.2722	0.2802	0.4141	0.1614	0.0163	0.1782	0.0785	19.98
	No 14	0.0970	18.4975	0.2722	0.2802	0.4141	0.1614	0.0163	0.1782	0.0785	20.00
	No 21	0.0218	14.2100	0.0957	0.2784	0.0619	0.0408	0.0054	0.0540	0.0221	14.79
25	No 15	0.1017	5.8678	0.0487	0.1695	0.1245	0.0537	0.0087	0.0310	0.0278	6.43

Table 2 Cancer risk analysis at the study site. Data for individual VOCs are cancer health risks (R_i) as calculated in Eq. (5), and data for total cancer risk are modified joint cancer health risks (R_j) as calculated in Eq. (6)

Distance to excavation point (m)	Sample	Cancer risks										Total
		1,1-dichloroethylene	1,2-dichloroethane	Chloroform	Benzene	Carbon tetra-chloride	Trichloroethylene	Tetrachloroethylene	1,1-dichloroethane	1,1,2-Trichloroethane		
1	No 3	0.0014	0.0122	0.0006	0.0001	0.0006	0.0002	0.0000	0.0001	0.0000	0.0152	
	No 9	0.0002	0.0122	0.0006	0.0001	0.0006	0.0002	0.0000	0.0001	0.0000	0.0140	
	No 16	0.0024	0.0494	0.0069	0.0001	0.0049	0.0009	0.0001	0.0011	0.0004	0.0660	
3	No 4	0.0014	0.0483	0.0008	0.0001	0.0066	0.0012	0.0001	0.0013	0.0005	0.0601	
	No 10	0.0023	0.0483	0.0008	0.0001	0.0066	0.0012	0.0001	0.0013	0.0005	0.0611	
	No 17	0.0013	0.0532	0.0080	0.0001	0.0039	0.0012	0.0001	0.0012	0.0004	0.0693	
5	No 5	0.0017	0.0569	0.0089	0.0001	0.0053	0.0014	0.0001	0.0013	0.0006	0.0763	
	No 11	0.0019	0.0569	0.0089	0.0001	0.0053	0.0014	0.0001	0.0013	0.0006	0.0765	
	No 18	0.0013	0.0428	0.0059	0.0001	0.0035	0.0008	0.0001	0.0008	0.0003	0.0556	
10	No 6	0.0013	0.0574	0.0081	0.0001	0.0048	0.0014	0.0001	0.0011	0.0006	0.0749	
	No 12	0.0011	0.0574	0.0081	0.0001	0.0048	0.0014	0.0001	0.0011	0.0006	0.0748	
	No 19	0.0006	0.0301	0.0033	0.0001	0.0017	0.0004	0.0000	0.0005	0.0002	0.0367	
15	No 7	0.0004	0.0421	0.0048	0.0001	0.0041	0.0010	0.0001	0.0006	0.0004	0.0537	
	No 13	0.0008	0.0421	0.0048	0.0001	0.0041	0.0010	0.0001	0.0006	0.0004	0.0540	
	No 20	0.0004	0.0318	0.0030	0.0001	0.0014	0.0004	0.0000	0.0004	0.0002	0.0376	
20	No 8	0.0008	0.0331	0.0037	0.0001	0.0037	0.0007	0.0001	0.0005	0.0003	0.0431	
	No 14	0.0010	0.0331	0.0037	0.0001	0.0037	0.0007	0.0001	0.0005	0.0003	0.0432	
	No 21	0.0002	0.0255	0.0013	0.0001	0.0006	0.0002	0.0000	0.0002	0.0001	0.0281	
25	No 15	0.0010	0.0106	0.0007	0.0000	0.0011	0.0002	0.0000	0.0001	0.0001	0.0139	

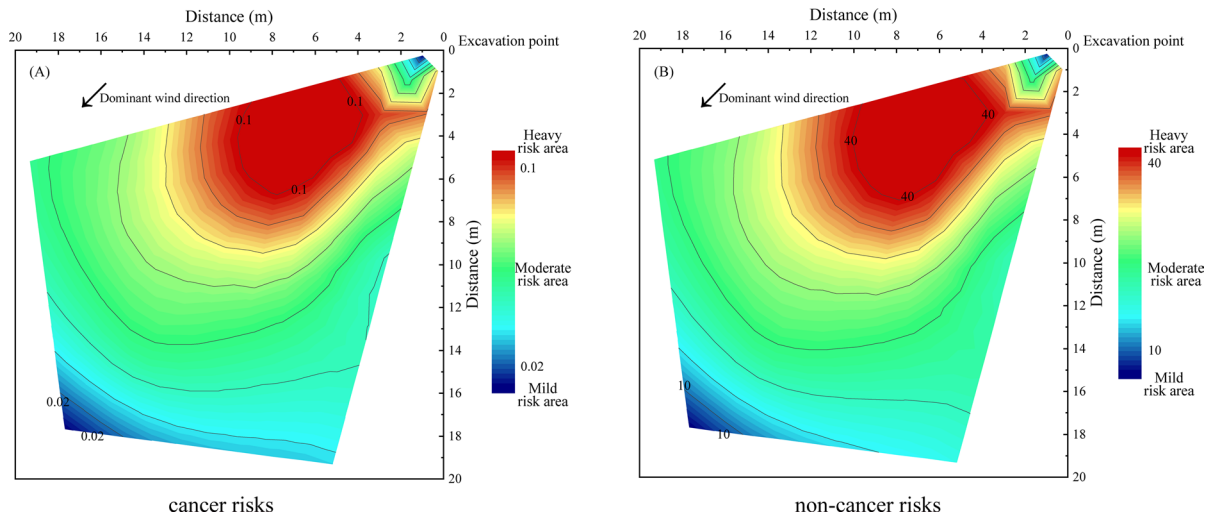


Fig. 2 Cancer **A** and non-cancer **B** risk distribution at the excavation site. **A** 0.10 and 0.02 represents the threshold for areas of heavy and moderate cancer risk, respectively. **B** 40

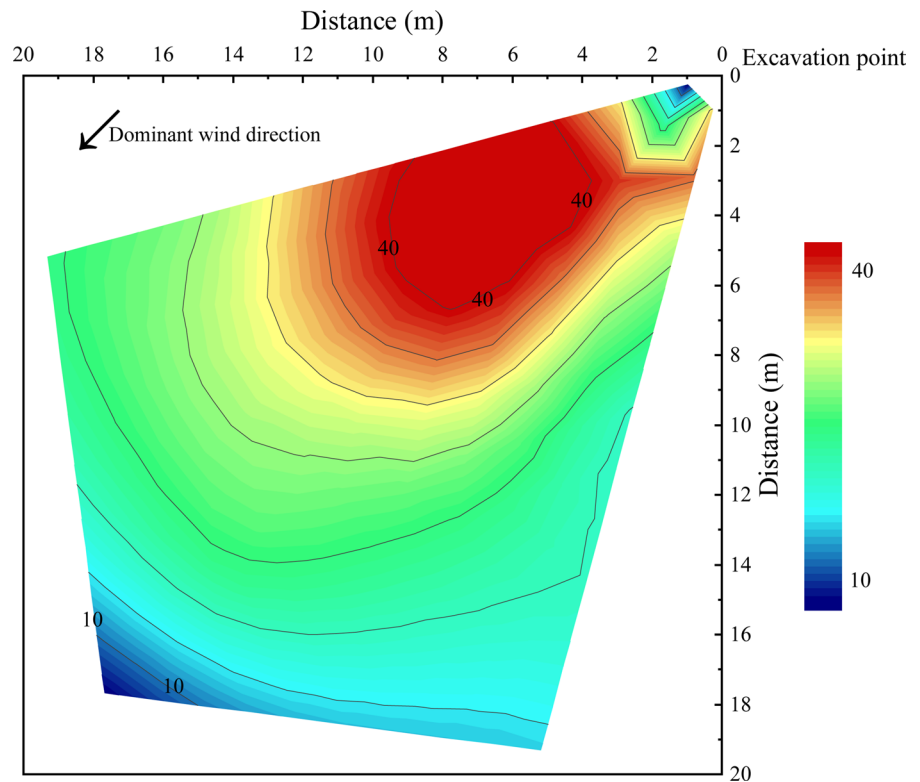
and 10 represent the threshold for areas of heavy and moderate non-cancer risk, respectively

dizziness, headache, and confusion at higher exposure levels (Jia et al., 2021). As for cancer risks, the contribution of 1, 2-dichloroethane was 74.4–90.8% and it is considered as the main factor with high carcinogenic risk among the dominant VOCs (Liu et al., 2020). Carbon tetrachloride (4.1–10.9%) and chloroform (1.3–11.7%) ranked as the second and third main carcinogenic toxic substances. de Los et al. measured the genotoxicity of shed oral mucosal cells and found that airborne particulate matters and VOCs represented by 1, 2-dichloroethane exert genotoxic effects on human (de Los et al., 2020). For chloroform exposure, non-carcinogenic effects are reported, including shortness of breath and inflammation of the nose and throat, convulsions, coma, and even death at high concentrations. A previous study also shows that those who survive acute exposure may develop liver insufficiency and kidney damage a few days later (Sekar et al., 2022). The total cancer risks ranged from 1.39×10^{-2} to 7.65×10^{-2} , significantly higher than the cancer risk standard (10^{-6} – 10^{-4}) suggested by US EPA (USEPA, 2005), showing the high human health risks at the excavation site.

Rapid risk identification and assessment during remediation excavation

For health risk control and protection, the application of rapid risk identification and evaluation is important at different points on the field (Huang et al., 2021). The total VOCs distribution was real time measured by PID illustrated in Fig. 3. Comparing the cancer and non-cancer risk distribution (Fig. 2), the total VOCs distribution from PID analysis fitted well with the risk pattern. The critical PID data were 10 ppm and 40 ppm for different risk assessment, respectively. In the dominant wind direction, samples with PID data of 40 ppm were located at the points with 9 m distance to the excavation site, exactly the same as the heavy-risk-level distribution identified by the specialized measurement. At the points with 9 m to 26 m distance to the excavation site, PID data ranged from 10 to 40 ppm, responsive to the areas with moderate risk. For those sites with low TD-GC/MS results and mild risks, PID data were lower than 10 ppm. In other wind directions, similar relationships between PID data and cancer/non-cancer risks were observed. Kumar et al. used PID to detect TVOCs and BTEX concentrations in different seasons (summer and winter), and lifetime carcinogenic risk (LCR) of benzene exceeded the USEPA recommendation (1×10^{-6}), and the non-carcinogenic risk hazard entropy (HQ) was in the

Fig. 3 Photo-ionization detector (PID) measurement for TVOCs distribution at the excavation site. The line of 40 ppm and 10 ppm represents the threshold for heavy- and moderate-risk areas, respectively



acceptable range (Kumar et al., 2014). Seseña et al. used PID to monitor indoor air quality in a university laboratory and found that airborne TVOC concentrations were sometimes higher than the recommended values, although no significant non-carcinogenic risk was found (Seseña et al., 2022). Our study further compared PID data and SPA followed by TD-GC/MS, evidencing the feasibility of PID for rapidly monitoring on-site VOCs concentrations with assessment of human health risks.

Comparing the gold standard VOCs analysis via SPA followed by TD-GC/MS, PID analytical results had the high degree of consistency ($p < 0.05$, $R^2 = 0.9994$, Fig. 4). Similar to previous research (Xu et al., 2021b), though PID cannot give specific information on individual VOC, it achieves rapid measurement of total VOCs. The measurement and data acquisition of PID are almost real time and reliable, and it is therefore widely used for indoor and outdoor air quality evaluation (Portela et al., 2021; Raysoni et al., 2017). More importantly, Fig. 5 further illustrates the positive relationship between PID data and cancer/non-cancer risks ($p < 0.05$, $R^2 = 0.9992$ and 0.9959 , respectively).

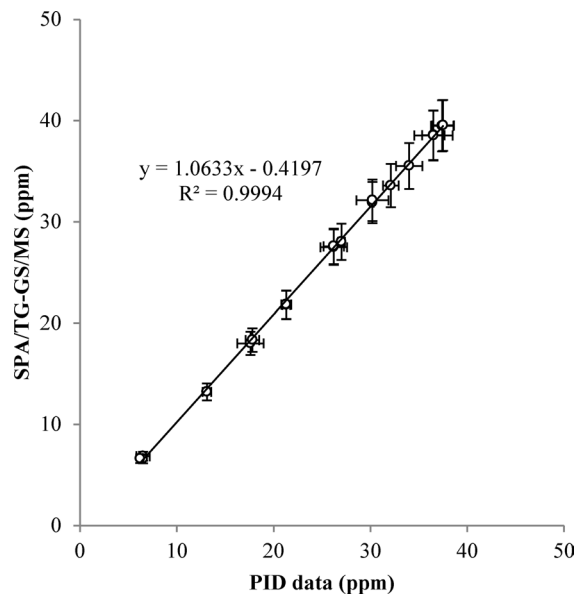


Fig. 4 Correlation analysis of PID and SPA/TD-GC/MS analytical data. PID refers to photo-ionization detector; SPA/TD-GC/MS represents solid-phase adsorption and thermal desorption gas chromatography–mass spectrometry

There were only limited previous investigations on the direct link between PID measured VOCs and human health (Jia et al., 2000), and this study initiated the feasibility that PID analytical method is an appropriate real-time detection tool to predict the level and distribution of cancer and non-cancer risks.

During the practical excavation activities, VOCs followed the dispersion of non-continuous air pollution plumes (Oliveri Conti et al., 2017), and their

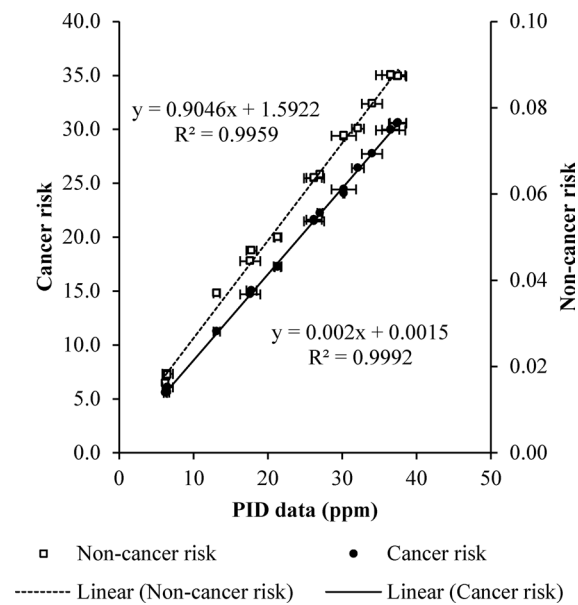


Fig. 5 Positive relationship between photo-ionization detector (PID) data and cancer/non-cancer risks. Squares are PID measurement data and risk model prediction; dashed and solid line represents regressions of non-cancer and cancer risks, respectively

synergistic health risks were hard to predict. The gold-standard calculation and assessment of the cancer and non-cancer risks were based on SPA and TD-GC/MS analysis of the major pollutants, which was a labor- and time-consuming technique (Lu et al., 2021). Many environmental factors, like the site topography, temperature, wind direction, and weather conditions, were variable, causing the uncertainties in human health risk evaluation (Xu et al., 2021a). From the results of this study, the PID technique was feasible to apply for rapid measurement and evaluation for the real-time health risks of total VOCs.

Criteria and control measures of different risk areas

Further actions for site risk management and control could be also suggested on the basis of PID data and risk areas, as listed in Table 3. Mild-risk area was identified with PID data less than 10 ppm, cancer risk less than 0.02, and non-cancer risk less than 10. The suggested simple protections included safety shoes, helmets, protective glasses, safety vests, construction gloves, and facemasks with adsorbent cartridges (Ari et al., 2022). The unprotected allowed access time was recommended as less than 8 h. For moderate-risk area, PID data ranged from 10 to 40 ppm, whereas the cancer and non-cancer risks were from 0.02 to 0.1 and 10 to 40, respectively. Besides the actions in the mild-risk area, further protections, like positive pressure respirators, disposable protective clothing, and earplugs, were recommended (Xuan et al., 2021). The unprotected allowed access time was suggested for no more than 60 min in this area. Heavy-risk sites exhibited PID data exceeding 40 ppm, cancer risk above 0.10, and non-cancer risk above 40. In this

Table 3 Criteria and control measures of different risk areas

Risk areas	Critical concentration by PID	Personal protective equipment	Unprotected allowed access time
Mild-risk	< 10 ppm	Safety shoes, helmets, protective glasses, safety vests, construction gloves, and masks	Less than 8 h
Moderate-risk	10 ppm to 40 ppm	Overall positive pressure respirators, disposable protective clothing, safety shoes, helmets, safety vest, earplugs (if required), protective glasses, and construction gloves	Less than 60 min
Heavy-risk	> 40 ppm	Immediately stop operation, evacuation of staff, to take measures to reduce pollutant concentration until pollutant concentrations restore to an acceptable level	Less than 15 min

Table 4 VOCs contamination components and concentrations at different sampling points. Data are concentrations of each VOCs at different sites (ppm)

Sample	1,1-dichloroethylene	1,2-dichloroethane	Chloroform	Benzene	Carbon tetrachloride	Trichloroethylene	Tetrachlorethylene	1,1-dichloroethane	1,1,2-Trichloroethane
No. 22	0.4830	21.8000	3.2600	0.1220	6.3400	0.1690	0.2450	1.9200	1.1300
No. 3	0.3260	5.4900	0.3230	0.0922	0.4830	0.0192	0.0750	0.1510	-
No. 4	0.3160	22.2000	0.4170	0.1210	5.1100	0.1180	0.1830	2.4700	0.9640
No. 5	0.4070	26.3000	4.5100	0.1200	4.0900	0.1450	0.2080	2.5500	1.1600
No. 6	0.2960	26.5000	4.1100	0.1520	3.7600	0.1460	0.2190	2.1400	1.2400
No. 7	0.0989	19.3000	2.4300	0.1390	3.1900	0.1040	0.1740	1.2300	0.8200
No. 8	0.1970	15.1000	1.9000	0.0980	2.8900	0.0751	0.1140	1.0400	0.5480
No. 9	0.0512	5.4900	0.3230	0.0922	0.4830	0.0922	0.0750	0.1510	-
No. 10	0.5440	22.2000	0.4170	0.1210	5.1100	0.1180	0.1830	2.4700	0.9640
No. 11	0.4490	26.3000	4.5100	0.1200	4.0900	0.1450	0.2080	2.5500	1.1600
No. 12	0.2630	26.5000	4.1100	0.1520	3.7600	0.1460	0.2190	2.1400	1.2400
No. 13	0.1860	19.3000	2.4300	0.1390	3.1900	0.1040	0.1740	1.2300	0.8200
No. 14	0.2260	15.1000	1.9000	0.0980	2.8900	0.0751	0.1140	1.0400	0.5480
No. 15	0.2370	4.7900	0.3400	0.0593	0.8690	0.0250	0.0605	0.1810	0.1940
No. 16	0.5580	22.7000	3.4900	0.0968	3.7800	0.0917	0.1350	2.1500	0.7660
No. 17	0.3080	24.5000	4.0400	0.1450	3.0500	0.1180	0.1550	2.3700	0.8340
No. 18	0.3140	19.6000	3.0100	0.0949	2.7400	0.0773	0.1080	1.6600	0.5890
No. 19	0.1420	13.7000	1.6800	0.0754	1.2900	0.0394	0.0634	0.8880	0.3070
No. 20	0.0962	14.5000	1.5200	0.1080	1.0600	0.0397	0.0689	0.7550	0.2990
No. 21	0.0507	11.6000	0.6680	0.0974	0.4320	0.0190	0.0377	0.3150	0.1540
No. 1	0.0134	9.0600	0.0951	0.1100	0.0166	0.0622	0.0253	0.0503	0.0558
No. 2	0.0134	7.5000	0.0702	0.0768	0.0107	0.0469	0.0127	0.0393	0.0407

region, there were high health risks and the unprotected allowed access time was restricted for less than 15 min. Moreover, the peaks of VOCs occurring in the dominant wind direction (Fig. 4) also required extra attention to minimize their risk to human health. In this case, the excavator operation should be stopped immediately for rapid response to mitigate VOC release until VOC levels dropped to the acceptable level. The appropriate mitigation activities were suggested as forced ventilation or spraying inhibitors (Bhat et al., 2021; Caron et al., 2020), and continuous PID measurement was suggested to monitor the variable total VOCs until they were less than 40 ppm. This work used PID data to determine areas of different risks with a single point emission, and future work should focus on multiple emission sources with the aid of both PID on-site measurement and VOCs emission models (Table 4).

Conclusion

This study addressed the control measures of human health risks caused by volatile organic compounds released by remediation excavation at an organic chemical contaminated site. A fast analytical method was developed using a photo-ionization detector to rapidly assess volatile organic compound contamination range and human health risks. Compared with time-consuming analytical methods of solid-phase adsorption and thermal desorption gas chromatography–mass spectrometry and model predictions, data from online photo-ionization detector successfully visualized the real-time contamination of total volatile organic compounds and fitted well with the human health risk distribution obtained by gas chromatography–mass spectrometry and model simulation. Photo-ionization detector simplified the identification of total volatile organic compound contamination, enabled rapid assessment of human health risks, and provided the feasibility of site management and rapid protection response at remediation excavation sites. In future research, photo-ionization detector can be applied to rapidly identify volatile organic compounds and semi-volatile organic compounds at the excavation site during *in situ* remediation processes at organic contaminated sites, such as coke fields and gas stations. In addition, some attempts can also focus on post-remediation assessment of contaminated sites using photo-ionization detector

to evaluate the long-term risks. Considering other key atmospheric contaminants at excavation remediation sites, particulate matters that possess risks to human health should also be addressed for their potential synergistic effects with volatile organic compounds in rapid assessment of human health risks.

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Declarations

Competing interests The authors declare no competing interests.

Conflict of interests The authors declare that they have no competing interests.

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Consent for publication Not applicable.

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