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RESEARCH ARTICLE

Real-time emission characteristics, health risks, and olfactory effects of VOCs released from soil disturbance during the remediation of an abandoned chemical pesticide industrial site

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Abstract

Volatile organic compounds (VOCs) released along with soil disturbance during the remediation of abandoned industrial sites have attracted great attention due to their possible toxicity and odour. However, the real-time emission characteristics of these VOCs and their subsequent effects on health and olfaction are less understood. In this study, the gaseous VOCs released from soil disturbance by excavators and drilling rigs at an abandoned chemical pesticide plant were monitored online with a laboratory-built single photoionization time-of-flight mass spectrometer (SPI-TOFMS). Twelve main VOCs with total mean concentrations ranging from 2350 to 3410 μg m^{-3} were observed, with dichloromethane (DCM) having a significant contribution. The total concentrations of the remaining 11 VOCs increased substantially during soil disturbance, with the total mean concentrations increasing from 18.65–39.05 to 37.95–297.94 μg m^{-3} and those of peak concentrations increasing from 28.46–58.97 to 88.38–839.13 μg m^{-3}. This increase in VOC concentrations during soil disturbance leads to an enhanced heath risk for on-site workers. The distinctive difference between the mean and peak concentrations of VOCs indicates the importance of using mean and peak concentrations, respectively, for risk and olfactory evaluation due to the rapid response of the human nose to odours. As a result, the cumulative noncarcinogenic risk at the relatively high pollutant plot was higher than the occupational safety limit, while the total carcinogenic risks at all monitored scenarios exceeded the acceptable limit. Among the VOCs investigated, DCM and trichloroethylene (TCE) were determined to be crucial pollutants for both noncarcinogenic and carcinogenic risks of VOCs. With regard to olfactory effects, organic sulphides, including dimethyl disulphide (DMDS), dimethyl sulphide (DMS), and dimethyl trisulphide (DMTS) were identified as dominant odour contributors (78.28–92.11%) during soil disturbance.

Keywords VOCs · Health risk · Olfactory effect · Contaminated site remediation · Mass spectrometer

Introduction

With the acceleration of urbanization and industrial restructuring, many enterprises with high energy consumption and high pollution that are located on the outskirts of cities have been shut down or relocated, leaving behind many contaminated sites. According to statistics, 342,000 contaminated sites have been identified in Europe (Panagos et al. 2013), and 450,000 to 600,000 registered sites have been contaminated by previous industrial activities in the USA (Song et al. 2019). In China, there are approximately 500,000 potentially contaminated sites in urgent need of management and remediation (Kan et al. 2021). Among them, abandoned chemical pesticide industrial sites are one of the main kinds of contaminated sites that easily cause

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severe environmental issues in the process of remediation (Kan et al. 2021). During routine operations, excavators and drilling rigs disturb the contaminated soil, potentially rapidly releasing large amounts of volatile organic compounds (VOCs) into the air, giving rise to acute or chronic poisoning of on-site workers and odour complaints from surrounding residents (Dumanoglu et al. 2014; Li and Yan 2022; Ma et al. 2016; Pranjic et al. 2018). Therefore, characterizing real-time VOC emissions and evaluating the corresponding health risks and olfactory effects are crucial to controlling secondary pollution and reducing their negative impacts during site remediation.

It has been reported that construction workers exposed to high levels of VOCs can suffer from acute or chronic toxicity, such as poisoning coma, respiratory and nervous system damage, sensory irritation, and cancer (An et al. 2014; Jia et al. 2021; Tong et al. 2018; Zhang et al. 2021a). To date, only a few studies have addressed VOC release and risk assessment during contaminated site remediation. Zhang et al. (2018a) evaluated the health risk during the remediation of polluted soils in northern China, indicating that restoration of VOC-contaminated sites may have serious risks for operating staff via respiratory exposure to chlorinated hydrocarbons, e.g. 1,2-dichloroethane and 1,1,2-trichloroethane. Zhao et al. (2020) investigated the characteristics and possible sources of VOCs in the atmosphere of a closed plant during the in situ desorption remediation process. The results showed that the concentration of total VOCs ranged from 99.49 to 849.63 μg m^{-3}, in which halogenated hydrocarbons (40.27%) and aromatics (39.73%) were the predominant compounds. Li and Yan (2022) studied the concentration, composition, and distribution of VOCs in different functional areas of a chemical site and found that the most polluted areas were pesticide production areas and that the substances with the highest concentrations were benzene series and halogenated hydrocarbons. To the best of our knowledge, a health risk assessment concerning the VOCs released from the remediation of chemical pesticide-contaminated sites has never been conducted.

The chemical pesticide industry is a major contributor to odour pollution; in addition, after its retirement, the chemical-contaminated site remains a secondary source of the odour, especially during site restoration. Odour gases can produce nausea and psychological influences on on-site workers and nearby residents (Palmiotto et al. 2014; Wang et al. 2021; Wenjing et al. 2015; Wu et al. 2018, 2017). To determine the prioritized odourants of polluted sources, the olfactory activity value (OAV), which is defined as the ratio of the concentration of a compound to its olfactory threshold, is often used to assess the olfactory effects of chemical compounds (Hayes et al. 2014; Lee et al. 2013; Sivret et al. 2016). This convenient assessment method has been applied by researchers to identify the main odourants in a wide variety of odourous sites, such as sludge composting plants (Han et al. 2018), wastewater treatment plants (Lewkowska et al. 2016), urban sewers (Sivret et al. 2016), and landfills (Wenjing et al. 2015). Nevertheless, the olfactory effects of VOCs released from the remediation of chemical pesticide-contaminated sites are less understood.

Traditional methods used to measure VOCs at contaminated sites are usually based on gas collection through summa canisters followed by off-line analysis with chromatographic techniques, e.g. chromatography (GC) with flame ionization detector (FID) or gas chromatography−mass spectrometry (GC−MS) (Duan et al. 2022; Sazakli and Leotsinidis 2020). These methods can provide accurate qualitative and quantitative results for the prepared samples. However, the collection time of a VOC sample usually takes several to tens of minutes (Fisher et al. 2018). By these methods, the VOC concentration obtained is equivalent to the average concentration over a period of time, which cannot reflect the real-time change in VOCs. In the actual scenario of site remediation, the operation of excavators and drilling rigs that dig the polluted soil may result in a rapid increase in the surrounding VOC concentrations and then change with the variation in air diffusion conditions, leading to a large difference between the mean and peak concentrations of VOCs in air. Considering that the human breathing time is only 1.6 s and that a burst of VOCs in the air inhaled by human breath may cause acute poisoning or olfactory sensory discomfort, the instantaneous peak concentration of VOCs is also a vital factor for risk and odour evaluation. Therefore, a rapid and online VOC analytical instrument is necessary for monitoring the real-time emission characteristics of VOCs during contaminated site remediation.

In this work, a laboratory-built single photoionization time-of-flight mass spectrometer (SPI-TOFMS) was used to directly detect the type and concentration of the VOCs emitted from a chemical pesticide-contaminated site during soil disturbance. The inhalation risk model recommended by the USEPA combined with Monte Carlo simulations was used to assess the health risks of toxic VOCs. The olfactory effects and the odour contribution of specific VOCs were evaluated based on their odour activities. The results of this study are helpful in systematically understanding the release behaviour, health risk, and odour nuisance effects of VOCs during soil remediation and provide scientific guidance for the reuse of similar polluted sites.

Materials and methods

Site description

The study was conducted at the former site of a chemical pesticide plant, which is located in the central part of

Suzhou, a large city in southeastern China. The company has been engaged in the production of chemical pesticides for more than 40 years. The main chemical products include phosphorous pesticides, chlorine-alkali compounds, 3-phenoxybenzaldehyde, chlorobenzenes, etc. The company closed and moved elsewhere in 2007, leaving an abandoned, contaminated site covering an area of 200,000 m^2. The area is basically flat, the soil texture is mainly silty clay and silty sand, and the underground water table is 0.9–5.0 m. During the site remediation process, VOCs released from the soil surface could cause sensory stimulation and health risks to on-site workers. In particular, the nauseating odours produced from soil disturbance by excavators and drilling rigs are often complained about by the surrounding residents.

Instrumentation

A laboratory-built SPI-TOFMS was used to monitor gaseous VOCs online in the ambient atmosphere. The structural schematic diagram of the instrument has been shown elsewhere (Wu et al. 2022). Briefly, it mainly consists of a vacuum ultraviolet (VUV) lamp, an ionizer, an ion migration lens, and a TOFMS. The VUV light was generated via the excitation of a rare gas (5% krypton in helium maintained at ~ 350 Pa) using a 13.6-MHz RF power supply running at 60 W. The central wavelengths of the VUV light are 116.9 nm (80%) and 123.6 nm (20%), corresponding to the photon energies of 10.0 and 10.6 eV, respectively. The photon flux of the VUV lamp focused on the ionization zone is ~ 10^{15} photons s^{-1}. The organic vapours in the air were sampled passively into the ionizer via the vacuum of the instrument with a sample flow rate of ~ 3.3 cm^3 s^{-1}. The ion migration lens consists of a set of electrostatic plates, which are orthogonal to the TOFMS. The TOFMS is V-type with a flight distance of 500 mm. The mass resolution (m/Δm) of the TOFMS at m/z 78 is ~ 800. The detection limit (LOD) of the instrument towards gaseous benzene is ~ 7 pptv in a 10-s acquisition time. Before each test, a standard gaseous sample (10 ppbv benzene) was measured to calibrate the detection sensitivity of the instrument.

Experimental procedure

The experiments were performed from May to June 2021, when the local surface temperature was 22–32 °C, and the relative humidity of the air was 60–80%. To investigate the variation in VOC emissions caused by soil disturbance during site remediation and its impact on human health, the SPI-TOFMS was moved to the construction site adjacent to the excavators and drilling rigs. During excavator and drill rig operations, the ambient air 1.5 m above the ground was sampled using a stainless steel tube (1/8 in. (inner diameter) × 5 m (length)) and measured directly by the SPI-TOFMS. A particle filter was installed at the front of the sampling tube to prevent dust from entering the instrument. A pump connected to a rotameter was installed at the end of the sampling tube to facilitate the flow of gaseous samples in the sampling tube. The sampling flow rate was kept at 15 cm^3 s^{-1}. A portion of the gaseous sample in the sampling tube was introduced into the SPI-TOFMS through a tee joint upstream of the pump. To avoid the adsorption loss of VOCs, the sampling tube was heated to 90 ℃ with a heating belt.

In this study, VOC release processes of soil disturbance from the excavator and drilling rig at different sites were monitored three times, respectively. Each episode lasted approximately 20 min. The VOCs in the air were detected every 30 s, and each detection took 10 s. The soil samples of each disturbance site were collected and analysed with GC−MS. The detailed sample pretreatment and analysis methods are provided in the Supporting information (SI).

Health risk assessment

For assessment of the occupational health risk of VOCs emitted from the contaminated site, inhalation is considered the most important pathway of human exposure (Wu et al. 2018; Xiong et al. 2020; Zhang et al. 2022). Thus, the carcinogenic and noncarcinogenic risks were evaluated by the workers' inhalation exposure to VOCs in the air combined with the toxicological parameters and the risk assessment model recommended by the USEPA.

The time-weighted inhalation exposure concentration (EC, μg $m^{-.3}$), which was derived from the measured VOC concentration in air calibrated specifically for the exposure scenario being evaluated, was determined using Eq. (1)

$$EC = \frac{CA \times ET \times EF \times ED}{AT} \quad (1)$$

where EC represents the exposure concentration for each compound (μg m^{-3}); CA is the measured concentration of VOCs in the air (μg m^{-3}); ET is the exposure time (7.5 h day^{-1}); EF is the exposure frequency (330 days $year^{-1}$ for workers); ED is the exposure duration (30 years for workers); and AT is the average lifetime (74.8 years × 365 × 24 = 655,248 h). The values of the exposure parameters ET, EF, and ED are derived from the interview data of Chinese construction workers (Tong et al. 2018). It should be noted that there are some assumptions in the risk assessment model. For example, the ED represents the number of years a worker will work in his profession. It is assumed that although EC refers to the concentration detected in 2021, the concentration measured in this case is still representative to some extent when the workers move from this contaminated site to other contaminated sites with a similar pollution level. These assumptions are widely used

in risk assessments (Tong et al. 2018; Zhou et al. 2011; Xiong et al. 2020).

The hazard quotient (HQ) and hazard index (HI) for specific VOC species used to express the chronic noncarcinogenic risk were calculated by Eqs. (2) and (3).

$$HQ = \frac{EC}{RfC \times 1000} \tag{2}$$

$$HI = \sum HQ \tag{3}$$

where RfC represents the toxicity reference concentration (mg m^{-3}).

The carcinogenic risk (CR), which is defined as the probability of inducing cancer during a lifetime, was calculated by Eq. (4).

$$Risk = IUR \times EC \tag{4}$$

where IUR represents the inhalation unit risk (μg $m^{-3})^{-1}$. The relevant parameters for risk assessment are listed in Table S3 of the SI.

In this study, a hybrid strategy was applied for health risk assessment, i.e. the deterministic (point estimation method) and random exposure assessment (Monte Carlo simulation) were used to assess the noncarcinogenic and carcinogenic risks of toxic VOCs, respectively (Civan et al. 2015; Xiong et al. 2020). For noncarcinogenic risk, the derived value HQ < 1 means no chronic toxicity, while HQ > 1 indicates a possible chronic health hazard after long-term exposure. For carcinogenic risk, the CR values were predicted to be $< 1.0 \times 10^{-6}$, $1.0 \times 10^{-6} \sim 1.0 \times 10^{-5}$, $1.0 \times 10^{-5} \sim 1.0 \times 10^{-4}$, and $> 1.0 \times 10^{-4}$ represent "negligible risk", "possible risk", "probable risk", and "definite risk", respectively (Nie et al. 2018; Wang et al. 2021; Zhang et al. 2018b).

Uncertainty and sensitivity analysis

To quantify the uncertainty and its impact on the carcinogenic and noncarcinogenic risks caused by soil disturbance, Monte Carlo simulation and sensitivity analysis were performed using Crystal Ball software (v.11.1.2.4.600) (Mishra et al. 2021). In this probabilistic modelling, the entire range of data was adopted, and different distributions were selected for input parameters. By using the Anderson−Darling goodness of fit test, the lognormal distribution was found to best fit the most VOC concentrations, which was similar to previous studies (Yang et al. 2019). The triangular distribution was used to describe the RfC and IUR, where the values of RfC and IUR recommended by the EPA were assigned to the most likely and maximum values, and the lowest risk zero was assigned to the minimum (Zhang et al. 2018b). The ET, ED, and EF parameters were fitted to a triangular distribution, and the AT followed a normal distribution. The values of the above parameters are listed in Table S4. To test the convergence and stability of the output, independent runs with 10,000 iterations and a 95% confidence interval were applied for simulation (Dai et al. 2017).

A sensitivity analysis was performed to determine the most significant parameter that influences the risk level. The result was represented by the rank correlation coefficients between input and output variables. A positive coefficient indicates a positive correlation between the variable parameter and the assessment result, while a negative coefficient indicates the opposite effect. The higher the absolute value is, the greater the impact on the estimated risk (Tong et al. 2018).

Olfactory effect analysis

The OAV_i and the odour contribution (PC_i) were calculated using Eqs. (5)-(7).

$$OAV_i = \frac{CA_i}{ODT_i} \tag{5}$$

$$SOAV = \sum OAV_i \tag{6}$$

$$PC_i = \frac{OAV_i}{SOAV} \tag{7}$$

where CA_i is the gaseous peak concentration of compound i (ppbv); ODT_i is the olfactory threshold of compound i (ppbv); SOAV represents the summed OAV_i of the mixture odourants; and PC_i is the percentage of the odour contribution of compound i (Wang et al. 2021).

Results and discussion

Real-time emission characteristics of VOCs

In this study, 12 main VOCs in the ambient air of the experimental sites were detected online with SPI-TOFMS, and other VOCs with signal intensities too low to be analysed effectively were ignored. The 12 VOCs include dichloromethane (DCM), benzene (Ben-), chlorobenzene (CB), dimethyl disulphide (DMDS), dimethyl sulphide (DMS), dimethyl trisulphide (DMTS), ethylbenzene (EB), *m,p*-xylene (*m,p*-Xyl-), *o*-xylene (*o*-Xyl-), styrene (Sty-), trichloroethylene (TCE), and toluene (Tol-). Considering that the SPI-TOFMS cannot discriminate isomers, the gaseous concentrations of EB, *o*-Xyl-, and *m,p*-Xyl-, which have the same molecular weight of 106, were determined from the total signal of m/z 106 observed by SPI-TOFMS distributed according to their relative abundance in soil, ionization

cross sections, and vapour pressures. The detailed calibration method is provided in the SI. Figure 1 shows the emission profiles of VOCs produced before, during, and after excavator and drilling rig disturbance, taking EB and DMDS as examples. ED1–3 and RD1–3 represent the three times of excavator disturbances and three times of drilling rig disturbances at different sites, respectively. The pink-covered part shown in Fig. 1 represents the duration from the beginning to the end of the disturbance.

As shown in Fig. 1, when the disturbance began, the air concentrations of EB and DMDS increased rapidly, and after the disturbance ended, their concentrations gradually returned to the background level. During soil disturbance, the pollutant concentration fluctuates with the variation in air diffusion conditions, e.g. instantaneous wind speed. Because the excavator and drilling dig had been warming up for a certain time before soil disturbance and the variation in the concentration from different VOCs had the same trend, the measured gaseous VOCs were thought to mainly result from the release of organic pollutants in the soil rather than from the exhausts of excavators and drilling machines. Furthermore, the released VOCs in the soil may be derived from the soil gas where the organic compounds have been in a three-phase equilibrium, which leads to a rapid release of VOCs showing a similar emission pattern when the disturbance starts. As shown in Fig. 1c, the concentration of VOCs released from scenario ED3 was much higher than those produced from other disturbance processes, which may partially result from the higher pollutant concentrations in the soil and the special soil properties at site ED3. The concentrations of organic pollutants in the soil in the ED1–3 and RD1–3 regions are provided in Table S5.

The mean and peak concentrations of VOCs measured before and during excavator and drilling rig disturbances at different sites are shown in Table 1. The total mean concentration ranges of the 12 VOCs before and during soil disturbance were 2350–3105 μg m^{-3} and 2638–3410 μg m^{-3}, respectively. Among these VOCs, DCM has a considerable contribution (91–99%) to the total emissions, with a mean concentration ranging from 2326 to 3112 μg m^{-3}. In addition, the concentration of DCM varied little throughout the monitoring process, which may be caused by the high concentration and strong volatility of DCM. As a common solvent, DCM is widely used in metal degreasing, varnishing strippers, adhesives, and pesticide production (Huang et al. 2014). It has been reported that the mean concentration of DCM released from the wastewater storage tank in a pesticide plant is 2309.55 μg m^{-3}, which is on the same order of magnitude as that observed in this study (Yang et al. 2019). DCM is also a typical volatile organic pollutant often detected in landfills and municipal solid waste (Zhang et al. 2021b).

As shown in Table 1, except for DCM, the total mean and peak concentrations of the remaining 11 VOCs clearly increased during soil disturbance. The total mean concentrations of these 11 VOCs released before and during soil disturbance were 18.65–39.05 and 37.95–297.94 μg m^{-3}, respectively, and those of peak concentrations were 28.46–58.97 to 88.38–839.13 μg m^{-3}, respectively. In comparison, there is a distinct difference between the mean and peak concentrations observed during the disturbance process due to the fugitive dilution of VOCs caused by the change in air diffusion conditions. In particular, the peak concentrations of some VOCs were significantly enhanced, e.g. the peak concentrations of DMDS and EB increased by 34 and 23 times, respectively, during the soil disturbance of scenario ED3. The mean concentrations of specific VOCs except DCM are 0.18–10.3 and 0.53–86.76 μg m^{-3} before

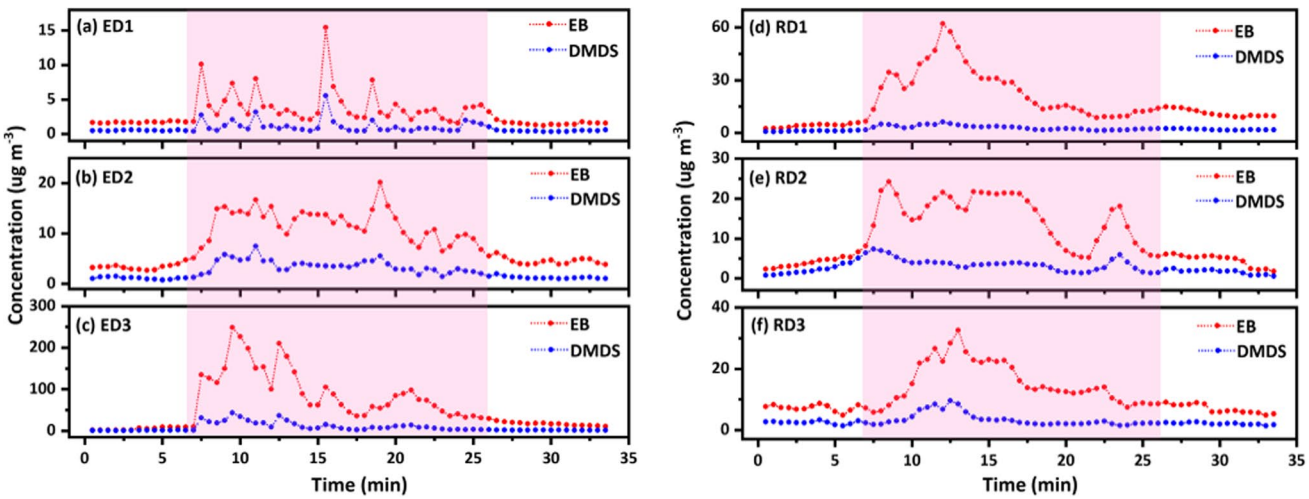

Fig. 1 Emission profiles of EB and DMDS produced before, during, and after excavator and drill rig disturbances monitored by SPI-TOFMS

Table 1 The mean and peak atmospheric concentrations of VOCs obtained before and during soil disturbance

Compounds	Mean concentrations before/during soil disturbance (μg m^{-3})						Peak concentrations before/during soil disturbance (μg m^{-3})					
	ED1	ED2	ED3	RD1	RD2	RD3	ED1	ED2	ED3	RD1	RD2	RD3
Ben-	2.34/3.97	2.50/3.68	1.29/2.50	2.02/5.19	2.32/5.95	2.65/4.92	3.55/12.28	2.81/6.76	1.51/5.39	2.56/17.87	3.19/12.06	3.15/12.41
EB	1.62/4.00	3.11/10.23	6.27/86.14	3.97/17.78	4.17/13.66	6.68/12.95	2.09/15.42	4.11/20.15	9.7/225.04	6.85/62.12	6.22/24.23	8.78/32.56
m, p-Xyl-	1.39/3.44	2.47/8.06	6.32/86.76	3.43/15.27	3.89/12.76	5.71/11.02	1.79/13.30	3.28/15.86	8.88/206.00	5.91/53.55	5.81/22.64	6.75/27.83
o-Xyl-	1.38/3.41	2.60/8.54	5.71/75.69	3.42/15.29	4.41/15.04	5.83/11.24	1.78/13.16	3.44/16.82	12.14/248.15	5.90/53.55	6.86/26.72	7.65/28.39
Tol-	5.09/4.19	2.79/3.16	2.19/5.71	1.94/3.29	2.75/7.08	1.90/2.54	3.4/7.12	3.34/4.03	2.61/15.19	2.23/8.28	4.31/14.3	2.35/4.61
CB	3.69/11.6	1.45/1.66	3.08/6.19	1.37/2.14	1.50/2.33	1.61/2.19	15.88/53.25	1.96/2.18	4.22/12.06	1.73/3.83	1.82/3.21	1.95/3.68
DMS	0.18/0.53	0.30/1.19	0.22/0.82	0.32/1.44	0.66/2.76	0.81/2.07	0.29/3.66	0.56/4.52	0.29/3.72	0.56/4.85	0.99/7.35	1.15/8.04
DMDS	0.48/1.10	1.06/2.87	0.94/10.9	0.87/2.40	1.41/3.50	1.91/3.19	0.6/5.56	1.47/7.47	1.26/43.46	1.25/6.11	2.22/7.35	2.74/9.60
TCE	3.40/4.15	4.47/5.32	10.30/12.30	5.16/6.02	4.03/5.32	4.39/5.27	4.5/7.51	5.49/7.45	11.77/16.53	5.94/8.12	4.85/7.45	5.20/7.68
DMTS	0.77/1.03	1.08/1.58	1.98/8.17	1.15/2.27	1.35/1.87	2.18/2.86	1.00/2.46	1.33/2.32	3.93/17.94	1.53/3.77	1.80/3.06	2.90/5.69
Sty-	0.48/0.53	0.42/0.56	0.74/2.76	0.42/0.81	0.42/0.74	0.45/0.70	0.80/0.85	0.68/0.82	1.16/6.90	0.55/2.05	0.58/1.11	0.53/1.33
Total 11 VOCs	18.65/37.95	22.26/46.85	39.05/297.94	24.07/71.90	26.91/71.01	34.12/58.95	35.68/134.58	28.46/88.38	58.97/839.13	35.00/224.10	38.65/129.48	43.90/141.83
DCM	2591/2733	2787/3016	3066/3112	2326/2566	2459/2751	2568/2707	2721/2901	2953/4125	3189/3208	2572/2709	2761/2953	2669/2982
Total 12 VOCs	2610/2771	2809/3063	3105/3410	2350/2638	2486/2822	2602/2766	2756/3036	2981/4213	3248/4047	2607/2934	2800/3082	2714/3124

and during mechanical operations, respectively. In general, the atmospheric background concentrations of 11 VOCs obtained in this study are lower than those of other chemical pesticide contaminated sites (35.8–724 μg m^{-3}) (Zhao et al. 2020). This result may be derived from the relatively low concentrations of organic pollutants in the soil of the plots investigated in this study. For example, the concentrations of benzene analogues in soil are in the range of several to dozens of milligrams per kilogram in some retired sites of chemical pesticide plants (Hu et al. 2021; Li and Yan 2022), which are 2–3 orders of magnitude higher than those obtained at the present site. It is worth noting that the remediation of those highly polluted sites could release much higher concentrations of VOCs into the air. One of the reference data is that the excavation of soil with VOC concentrations of 4.48×10^{-1} to 3.32×10^{2} mg kg^{-1} leads to VOC concentrations of 1900–26,500 μg m^{-3} in the air during the remediation of a chemical contaminated site (Zhang et al. 2018a).

Health risk assessment of VOCs

In view of the scene of site remediation, the health risk assessment was mainly focused on the estimation of the occupational health hazards of workers caused by the long-term inhalation of VOCs. Among the 12 VOCs detected, 8 species have chronic noncarcinogenic toxicity, and 4 species were confirmed carcinogens according to the USEPA database.

Noncarcinogenic risks

The estimated noncarcinogenic risks (the 5th, mean, median, and 95th percentiles) of specific VOC species before and during disturbance exposure are listed in Table S7. All of these VOCs have HQ values below 1, indicating that their noncarcinogenic risks are within the safe range. Since construction workers were exposed to a mixture of VOCs during site remediation, cumulative risks were also calculated using the mean values to represent the most likely scenario. Figure 2 shows the total HQs of 8 VOCs and the contributions of different compounds to the cumulative chronic toxicities. In general, the risks caused by VOCs during soil disturbance are higher than those caused by background VOCs. Due to the higher VOC concentrations, scenario ED3 has the highest cumulative health risks, which are 1.18 and 1.49 before and during soil disturbance, respectively. The HQ values exceeded 1, revealing that long-term exposure to VOCs at this site may have harmful effects on workers' health. With the exception of ED3, the cumulative risks for the other scenarios range from 0.69 to 0.91, with or without disturbance. An HQ value over 0.5 is considered a "likely concern" in some human health risk assessment reports

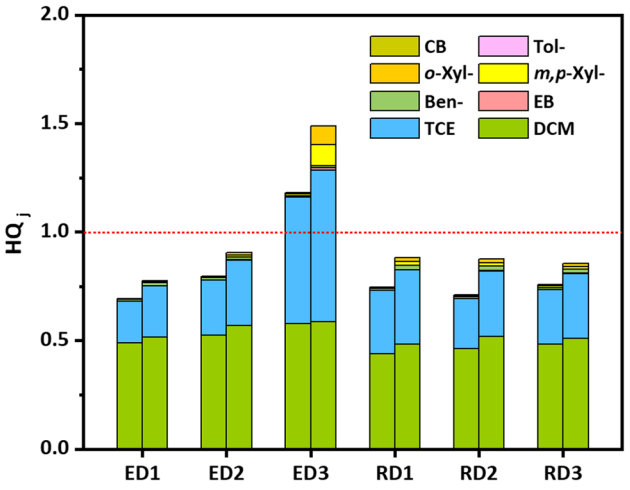

Fig. 2 Contributions of different compounds to the cumulative chronic toxicities

(Mustafa et al. 2017). Among the 8 health-related VOCs, DCM and TCE have the most important contributions to the cumulative noncarcinogenic risk, accounting for 39.5–70.5% and 27.7–49.3%, respectively, of the total HQ. Therefore, it is necessary to pay attention to the long-term health risks for workers caused by VOCs released during the remediation process of chemical pesticide-contaminated sites, especially DCM and TCE.

Carcinogenic risks

The probability distribution of the estimated inhalation cancer risk for the four carcinogenic VOCs (DCM, TCE, Ben-, and EB) released from scenario ED2 before (red bars) and during (blue bars) soil disturbance is shown in Fig. 3. The probability distributions of cancer risk for other scenarios are shown in Figs. S1–5. The average, median, and two percentiles (5th, 95th) cancer risks are provided in the box plot

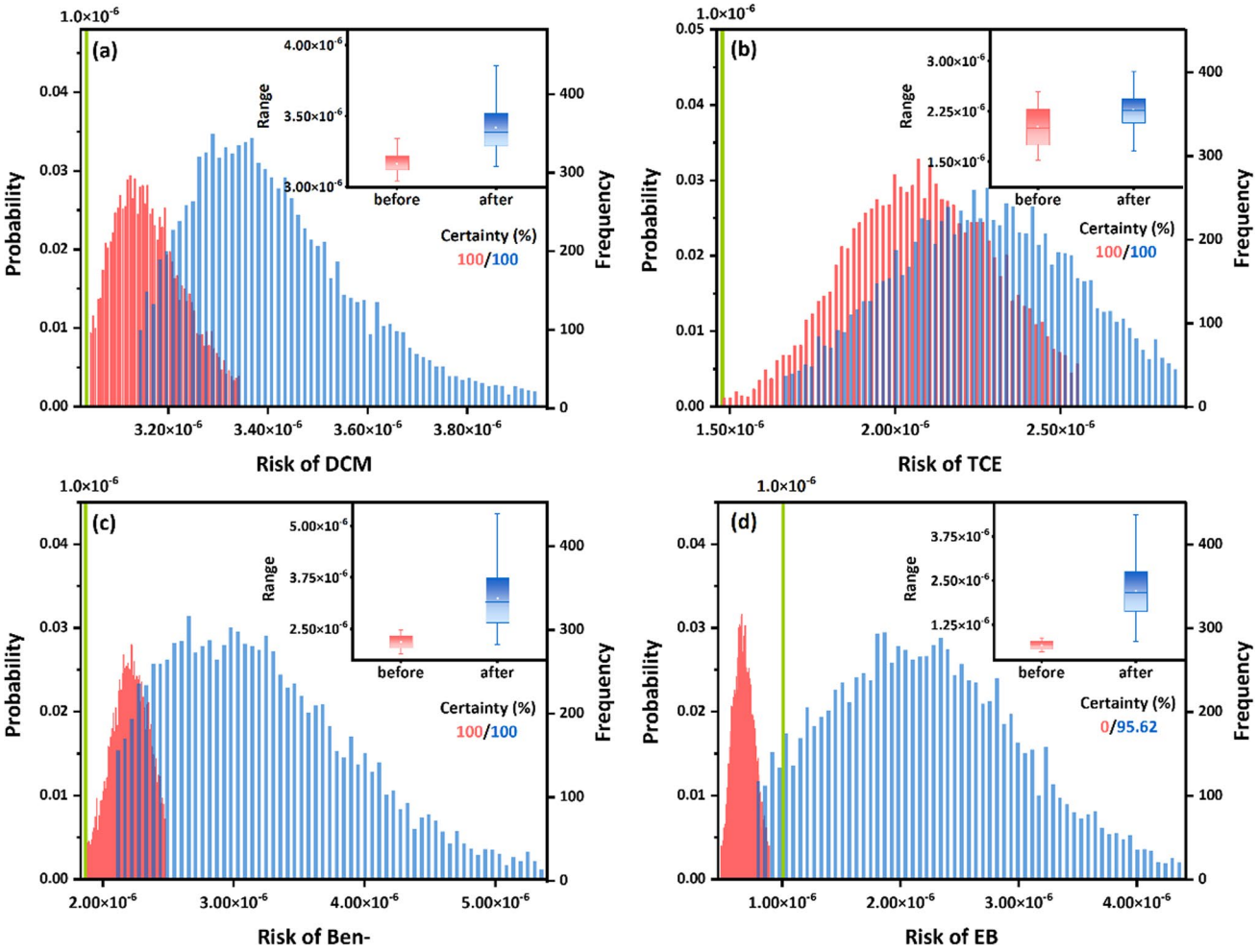

Fig. 3 Simulation results of the carcinogenic risks caused by DCM (**a**), TCE (**b**), Ben-(**c**), and EB (**d**) released from scenario ED2 before (red bars) and during (blue bars) soil disturbance

at the upper right corner of each figure. The green bar represents the EPA's acceptable cancer risk level (1.0×10^{-6}) for adults. The certainty level (%) shows the probability of cancer risk that exceeds the acceptable level.

From Fig. 3 and Figs. S1–5, the carcinogenic risk values follow a lognormal distribution. Overall, DCM and TCE presented a risk 100% above the acceptable value (1.0×10^{-6}) regardless of disturbance. For Ben-, the probabilities of risk that exceeded 10^{-6} were less than or equal to 100% before the disturbance and were 100% during the disturbance in all scenarios. The risk of EB during the disturbance was much higher than that before the disturbance. For example, as shown in Fig. 3D, the probability of risk exceeding 10^{-6} was 0% before the disturbance, while the probability increased to 95.62% during the disturbance. The mean values of carcinogenic risk are $(2.90–3.52)\times10^{-6}$ for DCM, $(1.93–5.72)\times10^{-6}$ for TCE, $(2.21–5.26)\times10^{-6}$ for Ben-, and $(1.13–24.38)\times10^{-6}$ for EB under different disturbance scenarios. It should be noted that all these risk values exceed the acceptable limit, and the total risk of the 4 VOCs is up to $(9.66–35.82)\times10^{-6}$, indicating that these compounds may pose carcinogenic risks to the workers operating the soil disturbance equipment. From a risk management perspective, the reduction of emissions of DCM, TCE, Ben-, and EB is recommended during the remediation of chemical pesticide industrial sites.

Uncertainty and sensitivity analysis

The results of the sensitivity analysis are shown in Fig. 4. The values of RfC and AT are negatively correlated with health risk, while other parameters are positively correlated. For DCM and TCM, the values of RfC and IUR have the greatest influence (> 50%) on the noncarcinogenic and carcinogenic risks, respectively, followed by the exposure time ED (ranging from 45 to 52%). For other VOCs, the exposure concentration influences the risk the most (52–83%), followed by RfC or IUR (33–52%). In comparison, CA is less influential than RfC or IUR on the risk of DCM and TCM, which may be the result of the lower variation in their concentrations observed during soil disturbance. Furthermore, ET, EF, and ED also have a substantial impact on risk

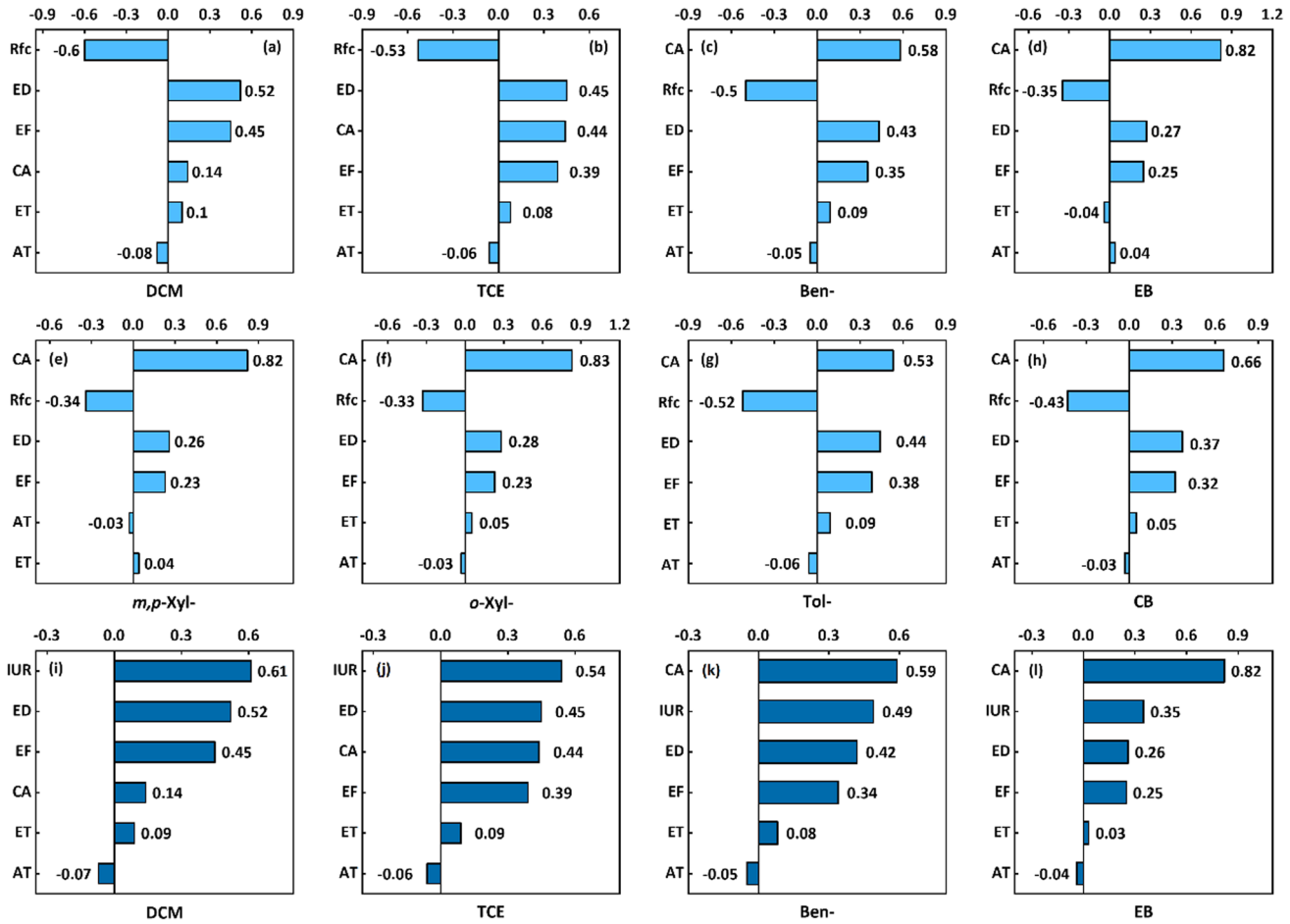

Fig. 4 Sensitivity analysis of noncarcinogenic risks (**a**–**h**) and carcinogenic risks for VOCs (**i**–**l**)

assessment, suggesting that some measures are necessary to reduce health risks, such as shortening exposure time and wearing protective equipment.

In this study, the uncertainties of risk assessment mainly arise from three aspects. First, the health risks were calculated only on the basis of VOC species detected with online SPI-TOFMS. Both carcinogenic and noncarcinogenic risks were likely to be underestimated because a certain species of VOC cannot be detected by SPI-TOFMS, such as some small molecule (C1 and C2) hydrocarbons and halogenated hydrocarbons with ionization energies (IEs) higher than the photon energy of VUV light (~ 10 eV). Second, the uncertainties may be due to the VOC concentrations observed during short-term monitoring, which does not include all construction scenarios, periods, sites, and environmental conditions. Finally, the values of RfC and IUR are usually obtained from the extrapolation of high-dose responses in animals, and there may be differences between the recommended and actual values, which also lead to potential uncertainties (Dai et al. 2017; Zhou et al. 2011).

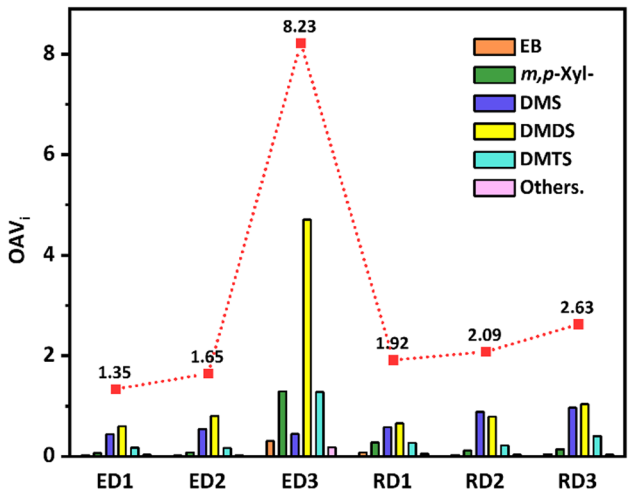

Fig. 5 OAV of odour substances from different scenarios. The red data points represent the total OVA

Olfactory effect analysis of VOCs

Considering that the peak concentrations of some odours are much higher than the mean concentrations observed in this study and that the human sense responds quickly to odours, the peak concentrations were used to calculate the OAVs of VOCs generated during soil disturbance. The OAV of each odour substance and the total OAV in different scenarios are shown in Fig. 5. The total OAVs for odourous substances emitted from ED1–3 and RD1–3 were 1.35, 1.65, 8.23, 1.92, 2.09, and 2.63, respectively. As expected, scenario ED3 had a much higher olfactory effect than the other scenarios. As shown in Fig. 5, in scenario ED3, the substances with the highest OAVs were DMDS and DMTS, while in the other scenarios, higher OAVs were observed for DMDS and DMS.

Figure 6 shows the contributions of the main odour substances to odour in different scenarios. Generally, DMDS (34.40–57.21%), DMS (5.44–42.45%), DMTS (10.08–15.63%), *m,p*-Xyl- (4.95–15.72%), and EB (1.43–4.01%) are major contributors to the odour during the remediation process of this abandoned industrial site. The main odourants identified in this study are also observed in a variety of other odour sources. In previous studies, organic sulphides (including DMS, DMDS, and DMTS) were determined to be priority odour pollutants in sewage sludge, landfill sites, and organic-rich waterbodies (Han et al. 2018; Nie et al. 2019; Tansel and Inanloo 2019). Benzene series (e.g. Ben-, Tol-, EB, and Xyl-) were observed as key odourants in a domestic waste landfill site (Wang et al. 2021).

Implication for practice

In this study, DCM and TCE were identified as two important pollutants that pose a threat to human health. In particular, it was observed that DCM had fairly high concentrations during the whole monitoring process for different scenarios. DCM and TCE were reported as two of the most frequently detected contaminants at USEPA superfund sites (Moran et al. 2007). However, relevant information

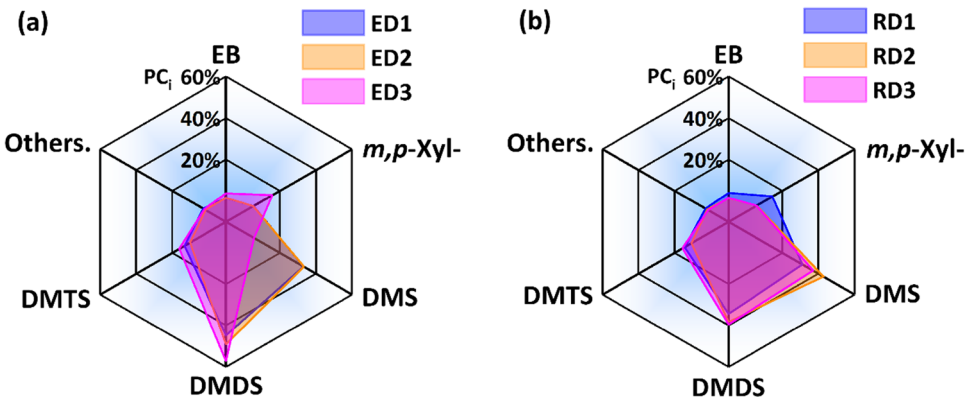

Fig. 6 Contributions of main odour substances to odour in scenarios of excavator disturbances (**a**) and drilling rig disturbances (**b**)

concerning DCM is limited in China (Huang et al. 2014). It has been reported that TCE (mean = 2581.29 μg m^{-3}) and DCM (mean = 2309.55 μg m^{-3}) presented the highest concentrations among the VOCs emitted from a pesticide wastewater storage tank (Yang et al. 2019). It is reasonable to infer that DCM may be a prevalent organic pollutant that subsists in many organic contaminated sites in China. According to the International Agency for Research and Cancer (IARC), DCM is classified as a possible carcinogenetic compound to humans (Group 2B). Long-term occupational exposure to DCM has been associated with numerous adverse health impacts on the body, such as the central nervous system, reproductive system, liver, and kidney toxicity levels (Olvera-Bello et al. 2010; Starr et al. 2006). Compared with other typical pollutants, such as the benzene series and aldehydes, DCM and TCE have a much higher olfactory threshold. Even at relatively high levels in ambient environments, these substances may be imperceptible to the human body. Hence, the health risk control of such substances should be a primary consideration in the remediation of organic contaminated sites. Regarding olfactory effects, to address odour-related complaints, attention should be given to organic sulphides (DMDS, DMS, and DMTS) at this site. Scavengers or masking agents are necessary to reduce the emission of these substances during soil disturbance.

Conclusions

The VOC emissions produced during soil disturbance by the excavator and drilling rig in an abandoned chemical pesticide industrial site were monitored online with an SPI-TOFMS. DCM was detected with high concentrations and had an overwhelming contribution to the total concentration of 12 main VOCs detected. The total concentrations of the remaining 11 VOCs increased obviously during soil disturbance, and the observed peak concentrations were much higher than their mean concentrations. The health risk assessment showed that the cumulative noncarcinogenic risk of the relatively high pollutant plot during soil disturbance was higher than the occupational safety limit. DCM and TCE are the two compounds that contribute the most to the noncarcinogenic risk, and their carcinogenic risks are above the acceptable limit at all monitored scenarios (disturbed or undisturbed). Sensitivity analyses indicated that the VOC concentrations and the RfC or IUR values have the greatest impact on the risk assessment. DMDS, DMS, and DMTS are the major odour contributors during soil disturbance. The results of this study may provide supplementary information for understanding VOC emission profiles and relevant influences during site remediation.

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Author contribution All the authors contributed to the study conception and design. Methodology, data collection and analysis, and writing–review and editing were performed by Haijie Wang and Bo Yang. The first draft of the manuscript was written by Bo Yang. Methodology, material preparation, and investigation were performed by Zitao Yan, Zuojian Zhang, Kui Jiang, Jin Yu, Yong Yang, Bo Yang, Jinian Shu, Zhangqi Yu, and Zhiyang Wei and all the authors commented on previous versions of the manuscript. All the authors read and approved the final manuscript.

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Data availability The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethical approval Not applicable.

Consent to participate Not applicable.

Consent to publish Not applicable.

Competing interests The authors declare no competing interests.

References

An J, Zhu B, Wang H, Li Y, Lin X, Yang H (2014) Characteristics and source apportionment of VOCs measured in an industrial area of Nanjing, Yangtze River Delta, China. Atmos Environ 97:206–214. https://doi.org/10.1016/j.atmosenv.2014.08.021

Civan MY, Elbir T, Seyfioglu R, Kuntasal ÖO, Bayram A, Doğan G, Yurdakul S, Andiç Ö, Müezzinoğlu A, Sofuoglu SC, Pekey H, Pekey B, Bozlaker A, Odabasi M, Tuncel G (2015) Spatial and temporal variations in atmospheric VOCs, NO_2, SO_2, and O_3 concentrations at a heavily industrialized region in Western Turkey, and assessment of the carcinogenic risk levels of benzene. Atmos Environ 103:102–113. https://doi.org/10.1016/j.atmosenv.2014.12.031

Dai H, Jing S, Wang H, Ma Y, Li L, Song W, Kan H (2017) VOC characteristics and inhalation health risks in newly renovated residences in Shanghai, China. Sci Total Environ 577:73–83. https://doi.org/10.1016/j.scitotenv.2016.10.071

Duan Z, Lu W, Mustafa MF, Du J, Wen Y (2022) Odorous gas emissions from sewage sludge composting windrows affected by the turning operation and associated health risks. Sci Total Environ 839:155996. https://doi.org/10.1016/j.scitotenv.2022.155996

Dumanoglu Y, Kara M, Altiok H, Odabasi M, Elbir T, Bayram A (2014) Spatial and seasonal variation and source apportionment of volatile organic compounds (VOCs) in a heavily industrialized region. Atmos Environ 98:168–178. https://doi.org/10.1016/j.atmosenv.2014.08.048

Fisher RM, Le-Minh N, Alvarez-Gaitan JP, Moore SJ, Stuetz RM (2018) Emissions of volatile sulfur compounds (VSCs) throughout

wastewater biosolids processing. Sci Total Environ 616–617:622–631. https://doi.org/10.1016/j.scitotenv.2017.10.282
Han Z, Qi F, Wang H, Liu B, Shen X, Song C, Bao Z, Zhao X, Xu Y, Sun D (2018) Emission characteristics of volatile sulfur compounds (VSCs) from a municipal sewage sludge aerobic composting plant. Waste Manage 77:593–602. https://doi.org/10.1016/j.wasman.2018.05.049
Hayes JE, Stevenson RJ, Stuetz RM (2014) The impact of malodour on communities: a review of assessment techniques. Sci Total Environ 500–501:395–407. https://doi.org/10.1016/j.scitotenv.2014.09.003
Hu G, Liu H, Chen C, Li J, Hou H, Hewage K, Sadiq R (2021) An integrated geospatial correlation analysis and human health risk assessment approach for investigating abandoned industrial sites. J Environ Manage 293:112891. https://doi.org/10.1016/j.jenvman.2021.112891
Huang B, Lei C, Wei C, Zeng G (2014) Chlorinated volatile organic compounds (Cl-VOCs) in environment - sources, potential human health impacts, and current remediation technologies. Environ Int 71:118–138. https://doi.org/10.1016/j.envint.2014.06.013
Jia H, Gao S, Duan Y, Fu Q, Che X, Xu H, Wang Z, Cheng J (2021) Investigation of health risk assessment and odor pollution of volatile organic compounds from industrial activities in the Yangtze River Delta region. China. Ecotoxicol Environ Saf 208:111474. https://doi.org/10.1016/j.ecoenv.2020.111474
Kan H, Wang T, Yu J, Qu G, Zhang P, Jia H, Sun H (2021) Remediation of organophosphorus pesticide polluted soil using persulfate oxidation activated by microwave. J Hazard Mater 401:123361. https://doi.org/10.1016/j.jhazmat.2020.123361
Lee HD, Jeon SB, Choi WJ, Lee SS, Lee MH, Oh KJ (2013) A novel assessment of odor sources using instrumental analysis combined with resident monitoring records for an industrial area in Korea. Atmos Environ 74:277–290. https://doi.org/10.1016/j.atmosenv.2013.04.001
Lewkowska P, Cieslik B, Dymerski T, Konieczka P, Namiesnik J (2016) Characteristics of odors emitted from municipal wastewater treatment plant and methods for their identification and deodorization techniques. Environ Res 151:573–586. https://doi.org/10.1016/j.envres.2016.08.030
Li Y, Yan B (2022) Human health risk assessment and distribution of VOCs in a chemical site, Weinan, China. Open Chem 20:192–203. https://doi.org/10.1515/chem-2022-0132
Ma Y, Du X, Shi Y, Hou D, Dong B, Xu Z, Li H, Xie Y, Fang J, Li Z, Cao Y, Gu Q, Li F (2016) Engineering practice of mechanical soil aeration for the remediation of volatile organic compound-contaminated sites in China: advantages and challenges. Front Environ Sci Eng 10:6. https://doi.org/10.1007/s11783-016-0870-x
Mishra H, Singh J, Karmakar S, Kumar R (2021) An integrated approach for modeling uncertainty in human health risk assessment. Environ Sci Pollut Res Int 28:56053–56068. https://doi.org/10.1007/s11356-021-14531-z
Moran M, Zogorski J, Squillace P (2007) Chlorinated solvents in groundwater. Environ Sci Technol 41:74–81. https://doi.org/10.1021/es061553y
Mustafa MF, Liu Y, Duan Z, Guo H, Xu S, Wang H, Lu W (2017) Volatile compounds emission and health risk assessment during composting of organic fraction of municipal solid waste. J Hazard Mater 327:35–43. https://doi.org/10.1016/j.jhazmat.2016.11.046
Nie E, Zheng G, Shao Z, Yang J, Chen T (2018) Emission characteristics and health risk assessment of volatile organic compounds produced during municipal solid waste composting. Waste Manage 79:188–195. https://doi.org/10.1016/j.wasman.2018.07.024
Nie E, Zheng G, Gao D, Chen T, Yang J, Wang Y, Wang X (2019) Emission characteristics of VOCs and potential ozone formation from a full-scale sewage sludge composting plant. Sci Total Environ 659:664–672. https://doi.org/10.1016/j.scitotenv.2018.12.404
Olvera-Bello AE, Estrada-Muniz E, Elizondo G, Vega L (2010) Susceptibility to the cytogenetic effects of dichloromethane is related to the glutathione S-transferase theta phenotype. Toxicol Lett 199:218–224. https://doi.org/10.1016/j.toxlet.2010.09.002
Palmiotto M, Fattore E, Paiano V, Celeste G, Colombo A, Davoli E (2014) Influence of a municipal solid waste landfill in the surrounding environment: toxicological risk and odor nuisance effects. Environ Int 68:16–24. https://doi.org/10.1016/j.envint.2014.03.004
Panagos P, Van Liedekerke M, Yigini Y, Montanarella L (2013) Contaminated sites in Europe: review of the current situation based on data collected through a European network. J Environ Public Health 2013:158764. https://doi.org/10.1155/2013/158764
Pranjic A, Oprckal P, Mladenovic A, Zapusek P, Urleb M, Turk J (2018) Comparative life cycle assessment of possible methods for the treatment of contaminated soil at an environmentally degraded site. J Environ Manage 218:497–508. https://doi.org/10.1016/j.jenvman.2018.04.051
Sazakli E, Leotsinidis M (2020) Odor nuisance and health risk assessment of VOC emissions from a rendering plant. Air Qual Atmos Health 14:301–312. https://doi.org/10.1007/s11869-020-00935-2
Sivret EC, Wang B, Parcsi G, Stuetz RM (2016) Prioritisation of odorants emitted from sewers using odour activity values. Water Res 88:308–321. https://doi.org/10.1016/j.watres.2015.10.020
Song Y, Kirkwood N, Maksimovic C, Zheng X, O'Connor D, Jin Y, Hou D (2019) Nature based solutions for contaminated land remediation and brownfield redevelopment in cities: a review. Sci Total Environ 663:568–579. https://doi.org/10.1016/j.scitotenv.2019.01.347
Starr TB, Matanoski G, Anders MW, Andersen ME (2006) Workshop overview: reassessment of the cancer risk of dichloromethane in humans. Toxicol Sci 91:20–28. https://doi.org/10.1093/toxsci/kfj145
Tansel B, Inanloo B (2019) Odor impact zones around landfills: delineation based on atmospheric conditions and land use characteristics. Waste Manage 88:39–47. https://doi.org/10.1016/j.wasman.2019.03.028
Tong R, Cheng M, Zhang L, Liu M, Yang X, Li X, Yin W (2018) The construction dust-induced occupational health risk using Monte-Carlo simulation. J Clean Prod 184:598–608. https://doi.org/10.1016/j.jclepro.2018.02.286
Wang Y, Li L, Qiu Z, Yang K, Han Y, Chai F, Li P, Wang Y (2021) Trace volatile compounds in the air of domestic waste landfill site: identification, olfactory effect and cancer risk. Chemosphere 272:129582. https://doi.org/10.1016/j.chemosphere.2021.129582
Wenjing L, Zhenhan D, Dong L, Jimenez LM, Yanjun L, Hanwen G, Hongtao W (2015) Characterization of odor emission on the working face of landfill and establishing of odorous compounds index. Waste Manage 42:74–81. https://doi.org/10.1016/j.wasman.2015.04.030
Wu C, Liu J, Zhao P, Li W, Yan L, Piringer M, Schauberger G (2017) Evaluation of the chemical composition and correlation between the calculated and measured odour concentration of odorous gases from a landfill in Beijing, China. Atmos Environ 164:337–347. https://doi.org/10.1016/j.atmosenv.2017.06.010
Wu C, Liu J, Liu S, Li W, Yan L, Shu M, Zhao P, Zhou P, Cao W (2018) Assessment of the health risks and odor concentration of volatile compounds from a municipal solid waste landfill in China. Chemosphere 202:1–8. https://doi.org/10.1016/j.chemosphere.2018.03.068
Wu X, Li Z, Shu J, Lu Z, Gao J, Yang B, Jiang K, Guo Y, Huang J (2022) Exploring breath biomarkers in BLM-induced pulmonary fibrosis mice with associative ionization time-of-flight mass spectrometry. Talanta 239:123120. https://doi.org/10.1016/j.talanta.2021.123120

Xiong Y, Bari MA, Xing Z, Du K (2020) Ambient volatile organic compounds (VOCs) in two coastal cities in western Canada: spatiotemporal variation, source apportionment, and health risk assessment. Sci Total Environ 706:135970. https://doi.org/10.1016/j.scitotenv.2019.135970

Yang K, Wang C, Xue S, Li W, Liu J, Li L (2019) The identification, health risks and olfactory effects assessment of VOCs released from the wastewater storage tank in a pesticide plant. Ecotoxicol Environ Saf 184:109665. https://doi.org/10.1016/j.ecoenv.2019.109665

Zhang K, Liu S, Wang S, Zhao M, Jia J (2018a) Health risk assessment and distribution of VOCs during excavation processes for the remediation of contaminated sites. Hum Ecol Risk Assess 25:2073–2088. https://doi.org/10.1080/10807039.2018.1488578

Zhang Z, Yan X, Gao F, Thai P, Wang H, Chen D, Zhou L, Gong D, Li Q, Morawska L, Wang B (2018b) Emission and health risk assessment of volatile organic compounds in various processes of a petroleum refinery in the Pearl River Delta, China. Environ Pollut 238:452–461. https://doi.org/10.1016/j.envpol.2018.03.054

Zhang K, Chang S, Fu Q, Sun X, Fan Y, Zhang M, Tu X, Qadeer A (2021) Occurrence and risk assessment of volatile organic compounds in multiple drinking water sources in the Yangtze River Delta region China. Ecotoxicol Environ Saf 225:112741. https://doi.org/10.1016/j.ecoenv.2021.112741

Zhang Y, Ning X, Li Y, Wang J, Cui H, Meng J, Teng C, Wang G, Shang X (2021b) Impact assessment of odor nuisance, health risk and variation originating from the landfill surface. Waste Manage 126:771–780. https://doi.org/10.1016/j.wasman.2021.03.055

Zhang L, Sun P, Sun D, Zhou Y, Han L, Zhang H, Zhu B, Wang B (2022) Occupational health risk assessment of the benzene exposure industries: a comprehensive scoring method through 4 health risk assessment models. Environ Sci Pollut Res Int 29:84300–84311. https://doi.org/10.1007/s11356-022-21275-x

Zhao X, Ma H, Lu J, Yin T, Zhang S, Zhang Q, Dong X, Shuai Q, Wei T, Gong X (2020) Characteristics and source apportionment of volatile organic compounds during the remediation of contaminated sites in Zhenjiang, China. Int J Environ Sci Technol 18:2271–2282. https://doi.org/10.1007/s13762-020-02947-y

Zhou J, You Y, Bai Z, Hu Y, Zhang J, Zhang N (2011) Health risk assessment of personal inhalation exposure to volatile organic compounds in Tianjin, China. Sci Total Environ 409:452–459. https://doi.org/10.1016/j.scitotenv.2010.10.022