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Risk-oriented source apportionment and implications for mitigation strategies of VOCs in industrial parks: Insights from odor pollution and health risks

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ABSTRACT

A typical industrial park in the upper reaches of the Yangtze River Economic Belt, which is 70 km from the Chongqing urban center, was used to investigate the occurrence and exposure of harmful volatile organic compounds (VOCs). An exposure risk method and a risk-oriented source apportionment approach were performed to assess the inhalation risks and apportion VOC sources, respectively. The quantitative relationships between risk factors and pollution sources were established, identifying key pathogenic and odorous VOCs. The quantitative emission reduction strategies were developed based on risk thresholds. Residents within the industrial parks face potential health risks due to pathogenic VOCs and nuisance odors, and workers in specific sectors experience two to six times higher risks than those in residential areas. Six risk sources were identified in the industrial park, ranked according to their contribution to VOC concentrations as follows: industrial sewage treatment (IST) (32.59 %), natural gas chemical industry (NGCI) (27.77 %), diesel vehicle exhaust (DVE) (12.04 %), pharmaceutical manufacturing industry (PMI) (11.14 %), chemical raw materials manufacturing (CRMM) (9.96 %), and iron and steel industry (ISI) (6.5 %). Among these, NGCI, IST, and CRMM were the top contributors to pathogenic risks, with contributions of 32.13 %, 29.71 %, and 21.71 % to non-carcinogenic risks, and 18.15 %, 19.87 %, and 27.99 % to carcinogenic risks, respectively. DVE produced significantly higher odor pollution compared to other sources, with intensities that were 3 to 10 times greater. The key pathogenic and odorous VOCs differ by source, resulting in varying control priorities for different VOC species. Reducing emissions from these six sources for 20 high-risk species (e.g., acrolein, 2-chlorotoluene, 1,2-dibromoethane, dichloromethane, and *p*-diethylbenzene) will simultaneously lower pathogenic and odor risks, with cumulative reduction rates ranging from 4.11 % to 93.75 %. This study provides quantitative control targets for VOCs from a health risk perspective, offering valuable guidance for developing risk management policies in industrial parks.

1. Introduction

Volatile organic compounds (VOCs) are organic compounds that easily evaporate and become gaseous at room temperature. VOCs not only considerably impact environmental air quality but also exhibit

toxicity, carcinogenic properties, and irritating odors, severely affecting public health and quality of life in surrounding areas (Duan et al., 2022; Zarra et al., 2019). Malodorous pollution, a typical nuisance, has recently emerged as a focus of public complaints in China (Jia et al., 2021). VOCs, as both air pollutants and significant odoriferous

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substances, have been a focus for researchers on health risks and odor pollution control (Cheng et al., 2019; Hsu et al., 2022; Hu et al., 2018; Li et al., 2020; Lu et al., 2015).

Epidemiological studies demonstrate that hazardous VOCs (H-VOCs) may cause cardiovascular and respiratory diseases, and certain VOC species have been implicated in cancer onset (Xiong et al., 2020). Research in VOC toxicology suggests that reductions in blood hemoglobin concentration, hematocrit, and platelet counts are associated with the presence of benzene, toluene, ethyl benzene, and xylenes (BTEX) in the blood (Chen et al., 2019; Cheng et al., 2022). A causal relationship has been established between benzene and tetrachloroethylene exposure and non-Hodgkin's lymphoma incidence (Rana et al., 2021). Furthermore, the International Agency for Research on Cancer (IARC) has definitively classified multiple VOC species, including 1,3-butadiene, dichloromethane, tetrachloroethene, and benzene, as carcinogenic to humans. In odor pollution research, odoriferous substances and VOCs are highly homologous. Apart from inorganic compounds, such as hydrogen sulfide and ammonia, most malodorous materials are also considered VOCs. Odorous VOCs (O-VOCs) are defined as VOCs that volatilize into gas and release unpleasant smells at room temperature. Organic sulfides, aromatics, and oxygenated compounds are generally regarded as the primary contributors to odor pollution, with some components detectable at exceptionally low threshold levels (Hu et al., 2020; Lin et al., 2023). Even at low concentrations, malodorous substances can have a profound adverse impact on public health and well-being. Many provinces and cities in China have incorporated malodorous pollution prevention into their "14th Five-Year Plan," emphasizing the management of VOCs as a priority and promoting coordinated control of both odors and VOC emissions.

As urban industrialization advances in China, industrial production activities have become the primary anthropogenic source of VOCs, accounting for over 50 % of total emissions (Simayi et al., 2019; Wu et al., 2016). Since 2000, industrial emissions have dominated the growth of VOC emissions in China. From 2000 to 2017, the VOC emissions from industrial manufacturing and solvent use grew considerably, with an annual average growth rate of 19.88 %. These two sources far exceeded other sources, such as transportation, energy consumption, residential fuel combustion, and waste disposal (Li et al., 2019). In the next 5 to 10 years, industrial VOC emissions in China will continue to rise, driven primarily by the use of VOC-containing products (Zhang et al., 2018). By 2030, the emissions will reach 24 Tg (Simayi et al., 2019). With increases in VOC emissions, complaints regarding industrial parks and nearby residential areas are also concerning. The complaints regarding odors account for over 20 % of all environmental complaints, and nearly 50 % of atmospheric environment complaints are in China (Liu et al., 2019). Gao et al. (2019) found that oxygenated VOCs (OVOCs) are the primary contributors to odor pollution in food processing plants, accounting for 79.6 % to 99.9 % of emissions. Hu et al. (2020) demonstrated that aromatic compounds, such as 1,4-diethylbenzene, *n*-propylbenzene, and *m/p*-xylene, are the most prevalent odor contributors in automotive parts and electrical product manufacturing plants, particularly during injection molding and spraying processes. Han et al. (2018) reported that benzene is the dominant odor compound from pharmaceutical and solvent spraying sources, while high levels of *o,m,p*-xylene characterize petrochemical sources, and halocarbons dominate emissions from oil refineries. These findings suggest that the odor VOC profiles of different industrial sources vary significantly. Thus, effectively identifying key odor species from different sources is critical for mitigating odor pollution and reducing associated health risks.

Industrial parks are primary platforms for modern social development and serve a crucial role in regional economic growth. However, the odorous pollution and health risks caused by emissions from these parks remain significant unresolved issues. According to the "China Population Environmental Exposure Behavior Pattern Research Report (Adult Volume)," approximately 110 million people live within a one-kilometer radius of industrial enterprises, including petrochemical, coking, and

thermal power plants (Jia et al., 2021). Both specialized industry workers and the general populace are exposed to olfactory sensory pollution and health risks via the inhalation of VOCs, necessitating ongoing scrutiny. While some studies have been conducted, they often address the issues of VOC odorous pollution and health risks as separate entities. Research on odor pollution typically focuses on the pollution sources, whereas health risk assessments are generally based on environmental receptor data (Duan et al., 2022; Li et al., 2020; Lu et al., 2015; Xiong et al., 2020). In this study, a risk-oriented source apportionment method was adopted in a comprehensive industrial park. This method assesses quantitative relationships of various risk factors between environmental receptors and pollution sources, identifies VOC species of high concern for pathogenicity and odor, and establishes a prioritized sequence for VOC control strategies. The results of this study prioritize VOC emission mitigation policies for industrial parks from a health risk perspective, thus providing guidance for the abatement of VOC emission in the industrial parks of China.

2. Materials and methods

2.1. Overview of the study area

The industrial system of the Yangtze River Economic Belt occupies half of the industries in China, and several manufacturing clusters with global impact have been formed along the Yangtze River. In this study, a typical industrial park located in the Yangtze River Economic Belt, which is 70 km from the Chongqing urban center, was selected as a representative example. Positioned in the core area of the upper Yangtze River, this industrial park is the largest national-level economic and technological development zone in this region, playing a vital role in driving regional economic growth. The industrial park covers an area of 73.6 km². The pillar industries include the iron and steel industry (ISI), pharmaceutical manufacturing industry (PMI), chemical raw materials manufacturing (CRMM), natural gas chemical industry (NGCI), and automobile manufacturing (AM). The industrial layout of the park aligns with the overall economic development direction of the Yangtze River Economic Belt, reflecting the comprehensive nature of the region's industrial structure. According to investigations, 164 enterprises within the industrial park are involved with atmospheric pollution. A residential town within the industrial park has a permanent population of approximately 30,000, including schools, hospitals, and residential areas. An urban center is located approximately 10 km northeast of the industrial park (Fig. 1). Residents frequently make complaints regarding air odor pollution issues in the industrial park. The diversified industrial layout results in complex VOC emissions, posing significant challenges to air quality management and public health, underscoring its typicality and research value.

2.2. Study framework

The research process is illustrated in Fig. S1. In this study, a comprehensive measurement of VOCs in the ambient air and stationary sources within the industrial park was conducted. The inhalation exposure risk of odorous and hazardous VOCs was assessed based on the U.S. Environmental Protection Agency's (EPA) risk assessment guidelines. Key steps included identifying high-risk VOC species, exposure assessment, dose-response analysis, and risk characterization. Multiple source identification methods were combined to determine major risk sources, their risk contribution levels, and key VOC species. The positive matrix factorization (PMF) model was employed to identify risk sources and quantify their risk contributions. Conditional bivariate probability function (CBPF) analysis was utilized to identify the spatial distribution of risk levels within the industrial park. The source profiles resolved by the PMF model were matched with measured source profiles to further validate the risk source apportionment results, and establish a quantitative relationship between environmental receptors and pollution

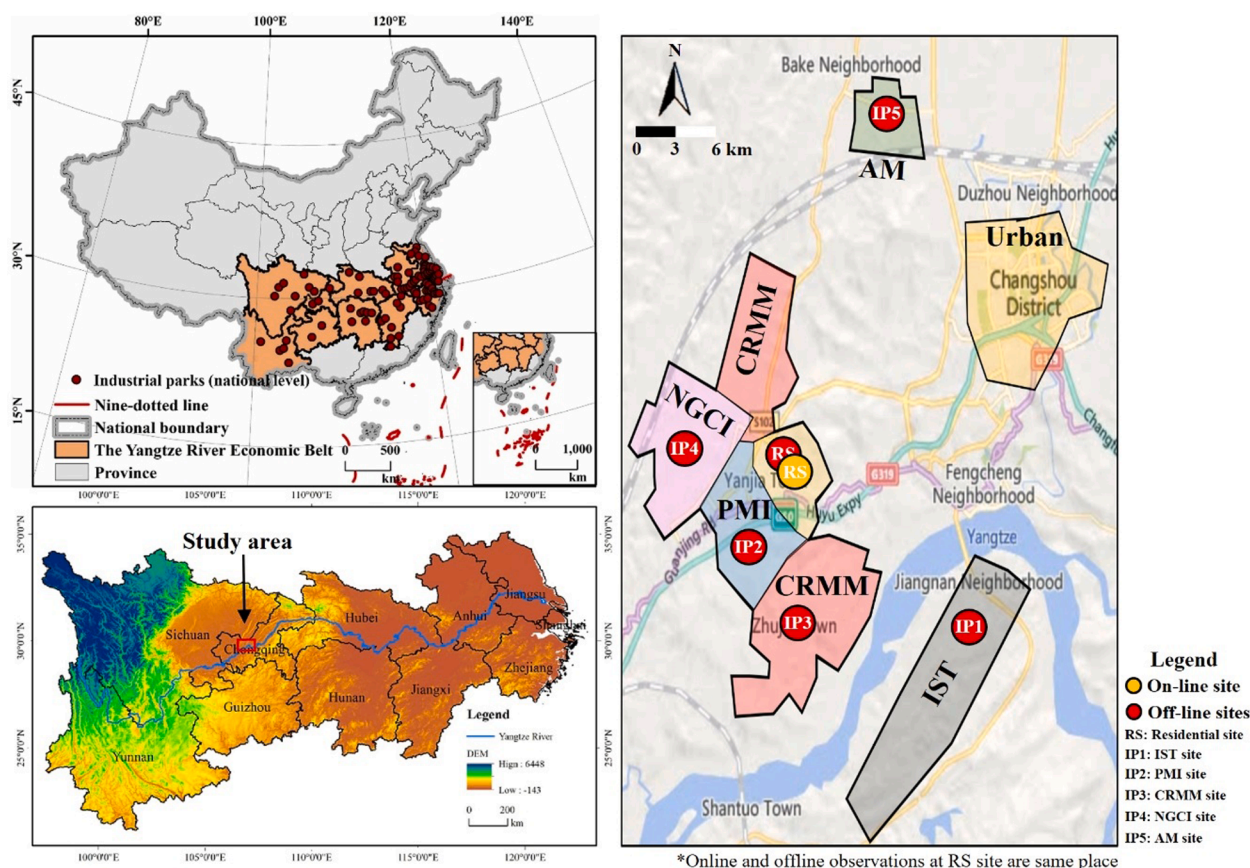


Fig. 1. Locations, industrial clusters, and distribution of VOC observation sites in the industrial park.

sources. Based on these steps, quantified mitigation strategies for each risk source were proposed. Each process is detailed as follows.

2.3. VOC sampling and analysis

2.3.1. High-resolution online measurement of VOCs

The atmospheric VOCs were continuously monitored using a gas chromatograph–mass spectrometer (Trace 1300-ISQ 7000, Thermo Fisher Scientific, USA) with a temporal resolution of 30 min from June 2021 to May 2022. 116 VOCs were identified and quantified, including 29 alkanes, 11 alkenes, 17 aromatics, 36 halocarbons, 21 OVOCs, acetylene, and carbon disulfide. The detailed species list is provided in Table S1 in supporting information (SI). The calibration curves for the target VOCs were constructed using a mixture of 57 photochemical assessment monitoring station (PAMS) standard gases (Linde Co., Germany) and the US EPA TO-15 standard (Spectra Gases Inc., USA). The calibration coefficients (R^2) for each VOC were consistently above 0.99, with detection limits (LOD) ranging from 0.11 to 0.99 ppb. The relative error (absolute value) for all target species was less than 10 % (from 0.03 % to 7.4 %). The relative standard deviation was below 10 % (from 0.7 % to 6.15 %). Detailed information is described in the literature (Li et al. 2023) and Text S1.

Additionally, to assess the significance of sulfur-containing compounds in the ambient air of the industrial park, data on sulfides and other inorganic compounds were collected from four monitoring stations within the park's environmental risk early warning and forecasting network. All four stations employed Fourier Transform Infrared (FTIR) spectrometers (RX-12-X, Mastek Technologies, China) for online monitoring, with a time resolution of 1 h. A total of 20 sulfur-containing compounds were monitored, including 16 sulfur-containing VOCs and 4 sulfur-containing inorganic compounds. Detailed information regarding the locations of the four stations, the analytical methods, and

the quality assurance and control procedures during the monitoring period is provided in Text S1. Data from the same period (June 2021 to May 2022) showed that the detection frequency of the 16 sulfur-containing VOCs was extremely low, with only carbonyl sulfide detected once at a mixing ratio of 71.92 ppb. It is noteworthy that some sulfur-containing organic compounds have extremely low odor thresholds (e.g., the odor threshold of ethyl mercaptan is less than 0.01 ppb), but current instruments struggle to achieve such low detection limits. This may overlook concentrations of sulfur-containing organic compounds that fall between the odor threshold and the detection limit. Moreover, our investigation of the production processes in the industrial park revealed that due to strict odor control policies implemented in recent years, many sulfur-related processes have been replaced or eliminated to limit sulfurous odor emissions. In summary, we conclude that sulfur-containing organic compounds have a minimal impact on the ambient air concentrations and odor in the industrial park. Therefore, sulfur-containing VOCs were excluded from the data analysis and evaluation presented in the “3 Results and Discussion” section of this study.

2.3.2. Offline VOC measurements from stationary sources

The chemical profiles of key VOC emission segments for five leading industries (ISI, PMI, CRMM, NGCI, and AM) were investigated in the industrial park. Measurements of stationary sources were divided into stack and fugitive emissions. The sampling sites are primarily located at stacks and production workshops/lines involved in VOC emissions. Detailed sampling sites across these five industries are listed in Table S2. Environmental air VOC samples from the industrial clusters were collected at the central point of each sector, while offline and online residential samples were taken from the same location. Stack and fugitive emission samples were collected using Summa canisters and 2,4-dinitrophenylhydrazine (DNPH) absorber tubes/absorbents. These

samples were analyzed using a gas chromatography–mass spectrometry/flame ionization detector (GC–MS/FID; Agilent 7890A/5975C, USA) and high-performance liquid chromatography (HPLC, Shimadzu, Japan). Detailed information on the sample collection and analysis protocols, along with the stringent quality assurance and quality control procedures, can be found in Text S2. The analytical methods and targeted 122 VOC species are summarized in Table S1.

2.4. Odor activity values and toxicity assessment

2.4.1. Odor thresholds and intensities

Since the concentration level of odorants does not directly assess the strength of an odor, the odor activity value (OAV) is commonly used to describe the intensity of an individual odorant's smell (Chai et al., 2022; Duan et al., 2022; Xue et al., 2022). Among all VOC species measured in ambient air and at stationary sources in this study, 54 VOC species are identified as potential O-VOCs, and their odor thresholds are listed in Table S3. The OAV is defined as the ratio of a compound's mixing ratio to its odor threshold.

$$OAV_{\text{sum}} = \sum_{i=1}^n OAV_i = \sum_{i=1}^n \frac{CA_i}{OT_i} \quad (1)$$

where CA_i is the mixing ratio of odor species i , 1×10^{-6} ; OT_i is the odor threshold for species i , 1×10^{-6} ; OAV_i is the OAV for species i ; OAV_{sum} is the sum of the OAV for all assessed odor species.

2.4.2. Exposure risk assessment

Among all detected VOC species in this study, 46 were identified as H-VOCs by five authoritative databases, as listed in Tables S4 and S5. Non-carcinogenic and carcinogenic risks were calculated using Equations (2) and (3), respectively:

$$HI = \sum_{i=1}^n HQ_i = \sum_{i=1}^n \frac{C_i}{REL_i} \quad (2)$$

$$LCR = \sum_{i=1}^n LCR_i = \sum_{i=1}^n DOSE_{\text{daily}} \times CSF_i \times ASF_a \times \frac{ED_a}{AT} \times FAH, \quad (3)$$

$$DOSE_{\text{daily}} = C_i \times \left(\frac{BR}{BW} \right)_a \times A \times EF \times 10^{-6} \quad (4)$$

where HI and LCR denote the cumulative hazard index and lifetime cancer risk associated with hazardous VOCs, respectively. Typically, a HI greater than 1 and an LCR greater than 1×10^{-6} are considered unacceptable risk levels (Cheng et al., 2022; Xiong et al., 2022). HQ_i and LCR_i denote the hazard quotient and carcinogenic risk for species i , respectively. REL_i refers to the reference exposure level for species i , with specific values listed in Table S4. $DOSE_{\text{daily}}$ denotes the daily inhalation dose of hazardous VOCs (units: $\text{mg} \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$), calculated as the product of the concentration of species i (C_i , $\mu\text{g} \cdot \text{m}^{-3}$), normalized breathing rate (BR/BW , $\text{L} \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$), inhalation absorption factor (A , dimensionless), and exposure frequency (EF , %). CSF_i is the inhalation cancer slope factor for species i , which is dimensionless. ASF_a is the sensitivity factor, which is dimensionless. ED_a , AT , and FAH_a denote the duration of exposure (years), lifetime of exposure (years), and time spent at home (dimensionless), respectively. Parameters involved in Equations (3) and (4) for different age groups are listed in Table S5 and S6, based on guidance from OEHHA.

2.5. Risk-oriented source apportionment

2.5.1. Integrated contribution assessment of risk sources

A risk-oriented source apportionment method was used to quantify the impact of VOC emissions on odor pollution and human health. First, pollution sources were identified using the positive matrix factorization

model (PMF, version 5.0). The VOC species, parameter settings, and factor diagnostic scheme used in the PMF model are described in Text S3. For each identified source from the PMF model, we calculated the corresponding inhalation risks by combining source-resolved VOC mixing ratios with their respective toxicity values (cancer and non-cancer risk factors). Subsequently, based on the resolved source profiles by PMF, the percentage of species in each factor was used to quantify VOC sources' contributions to HI, LCR, and OAV.

$$RS_k = \sum_{i=1}^n k_i \times P_i \quad (5)$$

Here, RS_k is the cumulative contribution of risk factor k from a specific source. In this study, we calculated the RS_k values for three risk factors: OAV, HI, and LCR. k_i is the risk level associated with VOC species i , and P_i is the percentage contribution of VOC species i in the source profile as determined by PMF analysis.

To enhance the specificity of risk source apportionment in the industrial park, the PMF model's identification of industry sources was further refined to individual emission processes within each industry. These processes include emissions from workshops, production lines, storage tanks, raw material storage, and sewage treatment stations, including both stack and fugitive emissions. Detailed information on this theoretical approach can be found in Text S4. A multiple linear regression model was used to perform secondary matching between PMF-resolved industry source profiles and the measured profiles from various emission processes. The degree of matching was used to quantify the contribution of each process to the overall risk. This method helps validate the PMF source apportionment results and enhances their reliability. Furthermore, the refined results provide more targeted recommendations for emission control in industrial parks.

2.5.2. Conditional bivariate probability function (CBPF) analysis

The CBPF analysis was also used to validate risk source allocation results and explore the impact of risk sources under various wind directions and speeds (Song et al., 2021; Xiong et al., 2020). The CBPF can be calculated using Equation (6):

$$CBPF_{\Delta\theta, \Delta u} = \frac{m_{\Delta\theta, \Delta u} | C \geq x}{m_{\Delta\theta, \Delta u}} \quad (6)$$

where $CBPF_{\Delta\theta, \Delta u}$ represents the probability that the contribution from a risk source exceeds a threshold x within a specific wind direction interval $\Delta\theta$ and wind speed interval Δu . Then, $m_{\Delta\theta, \Delta u} | C \geq x$ denotes the number of instances where the target parameter in the intervals $\Delta\theta$ and Δu exceeds threshold x , and $m_{\Delta\theta, \Delta u}$ represents the total occurrences within these intervals.

2.5.3. Initial mitigation targets

We assessed the initial mitigation targets (IMTs) for hazardous VOCs and their sources in the industrial park to facilitate decision-making regarding appropriate VOC emission reduction strategies. IMTs may also be considered mixing ratios derived from reverse calculations based on risk levels, representing the maximum allowable mixing ratios of toxic VOCs at a specific site without threatening public health. The IMTs for hazardous VOCs and their sources were determined by rearranging Equation (7):

$$IMT_i = \text{Min} \left[\begin{array}{l} OAV_{\text{target}} \times OT_i, HQ_i \times REL_i, \\ \frac{LCR_{\text{target}} \times AT}{\left(\frac{BR}{BW} \right) \times A \times EF \times CSF_i \times ASF \times ED \times FAH \times 10^{-6}} \end{array} \right], \quad (7)$$

where OAV_{target} , HI_{target} , and LCR_{target} represent the target risk levels for odor pollution, non-carcinogenic, and carcinogenic risks, respectively. In this study, these values were set to 1, 1, and 1×10^{-6} .

After determining the IMT_i for specific VOC species, observation values (Obs) that exceed these targets during the monitoring period were screened. Using Equation (8), estimating the VOC reduction rates for hazardous VOCs and their sources at the lowest acceptable risk level is possible:

$$R_i = \frac{IMT_i - Obs}{Obs} \times 100\% \quad (8)$$

2.6. Uncertainty and sensitivity assessment

Risk assessment is often accompanied by inherent uncertainties, primarily due to the variability of specific parameters (e.g., C_i , OT, REL, EF, AT, A, and ED) in the calculation process (Cheng et al., 2022; Xiong et al., 2022). Monte Carlo simulations and Crystal Ball software were used in this study to quantify the uncertainties in health risk assessment. In addition, the PMF modeling used for source apportionment encompasses certain uncertainties. Atmospheric VOC exposure concentrations are suitably described by a log-normal distribution, while parameters such as OT, REL, EF, AT, and ED are commonly modeled using a triangular distribution (Du et al., 2014; Zhou et al., 2011). The standard deviation of C_i is derived from observational data, with the standard deviations of the risk assessment parameters and PMF-derived VOC source profiles set at 20 % and 30 % of their means, respectively. Each simulation involves 10,000 iterations to ensure the convergence and stability of the results. Furthermore, a sensitivity analysis prioritizes the significance of input assumptions in the risk assessment results, identifying the most influential sensitive input variables affecting the outcomes.

3. Results and discussion

3.1. Ambient VOC mixing ratios and composition

Based on a one-year monitoring of ambient VOC mixing ratios in the industrial park, the total VOC (TVOC) mixing ratio was an average of 142.79 ± 258.45 ppbv. The mixing ratios of H-VOCs and O-VOCs were 56.51 ± 110.21 and 87.07 ± 184.92 ppbv, representing 39.58 ± 20.94 % and 60.98 ± 22.26 % of TVOC, respectively (Fig. 2a). The alkanes constituted the largest component (39.05 ± 24.04 %), followed by

halocarbons (24.23 ± 22 %) and OVOCs (21.33 ± 20.13 %) (Fig. 2b). In the H-VOCs, halocarbons (56.56 ± 24.37 %), OVOCs (19.05 ± 21.08 %), and aromatics (18.29 ± 16.04 %) made significant contributions. Similar to the composition of TVOCs, alkanes were the predominant contributors to O-VOC (59.3 ± 25.95 %), followed by halocarbons (16.76 ± 19.73 %) and OVOCs (11.98 ± 15.01 %).

Propane was the highest mixing ratio, accounting for 27.58 ± 23 % of the TVOCs, followed by dichloromethane (9.45 ± 11.87 %), *trans*-1,3-dichloropropene (8.21 ± 0.14 %), butanal (3.01 ± 6.67 %), methyl *t*-butyl ether (MTBE, 2.85 ± 8.26 %), crotonaldehyde (1.88 ± 9.28 %), styrene (1.86 ± 2.11 %), acetone (1.74 ± 2.8 %), and benzaldehyde (1.5 ± 2.29 %). Propane also significantly contributed to the O-VOCs. Studies have shown that a high mixing ratio of propane is typically associated with domestic petrochemical parks, with substantial emissions regularly escaping during the use and extraction of fossil fuels. Dichloromethane, found in both H-VOCs and O-VOCs, primarily originates from industrial emissions. The industrial wastewater treatment systems in industrial parks may be significant sources of dichloromethane (Pitiriciu et al., 2021; Yang et al., 2019). MTBE, styrene, and acetone were also at high mixing ratios as H-VOCs or O-VOCs.

3.2. Emission characteristics of VOCs from stationary sources

Fig. 3 presents the chemical composition profiles of VOCs from different emission processes across five dominant industries within the industrial park. As shown in Fig. 3, the VOC compositions from emission processes in the ISI are similar to those detected at the factory center boundary (FCB), with the top ten VOC species primarily consisting of alkanes, alkenes, and aromatics. Overall, the major VOCs in these emission processes and at the FCB include ethane, *iso*-pentane, ethylene, ethyne, benzene, toluene, *m/p*-xylene, and naphthalene, with cumulative contributions ranging from 31.83 % to 66.13 %. In the PMI, ethanol and 2-butanone dominate the VOC profiles from workshop outlets, contributing over 70 %. Although ethanol and 2-butanone have lower contributions in fugitive emissions from workshops, other characteristic species from the PMI, such as *iso*-propanol, acetaldehyde, and acetone, also show high contributions. Similarly, ethanol and 2-butanone are major contributors at the FCB, with respective contributions of 16.56 ± 5.16 % and 20.39 ± 7.53 %. Additionally, dichloromethane (18.97 ± 4.45 %) shows significant contributions, likely influenced by emissions of sewage treatment, where dichloromethane is the primary VOC in PMI sewage emissions, contributing 60.65 ± 12.88 %.

The VOC profiles for stack and fugitive emissions in CRMM vary

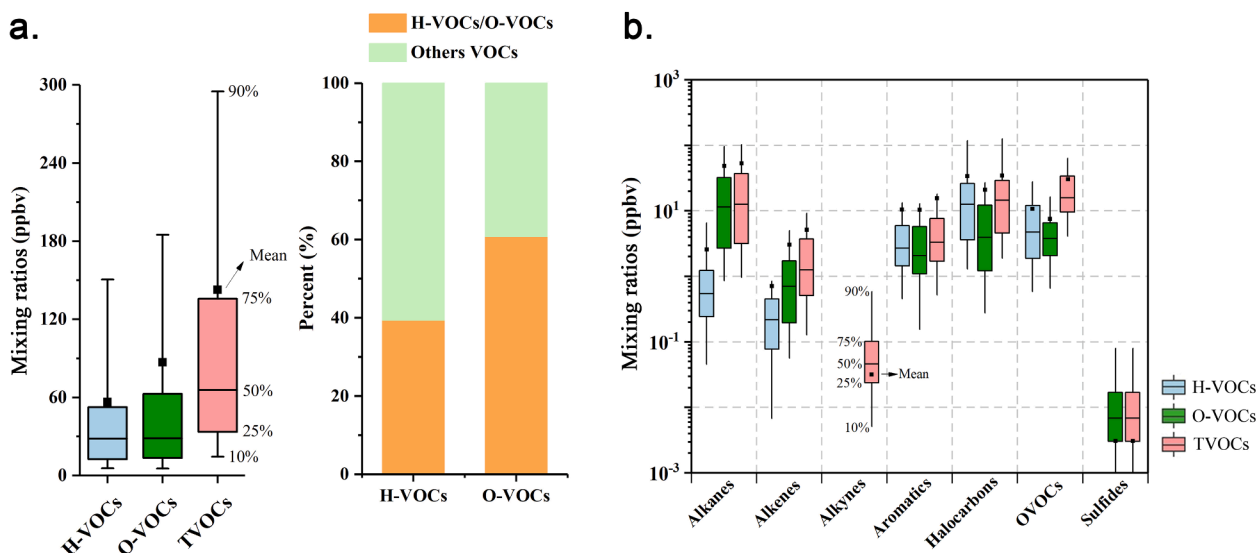


Fig. 2. Mixing ratio distributions of TVOCs, H-VOCs, and O-VOCs and their respective VOC groups during the observation period.

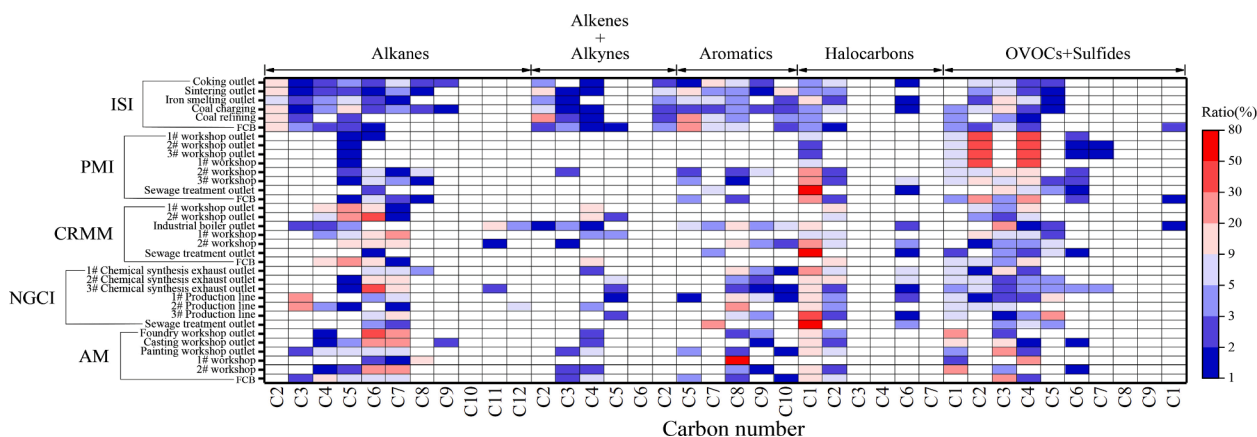


Fig. 3. Source profiles of VOCs from various emission processes in five dominant industries within the industrial park.

significantly. Stack emissions are dominated by *n*-pentane, vinyl acetate, 1,3-butadiene, 1,2-dibromoethane, and butane, while fugitive emissions are dominated by dichloromethane, MTBE, *p*-dichlorobenzene, *o*-dichlorobenzene, and styrene. Due to the semi-enclosed workshop conditions in CRMM, the detected fugitive VOCs may be influenced by external factors. Thus, the presence of dichloromethane in fugitive emissions is likely influenced by sewage treatment processes in CRMM.

In NGCI, the VOCs from organized emissions are dominated by halogenated hydrocarbons and C4-C7 alkanes, such as dichloromethane, 2,3-dimethylbutane, 2-methylpentane, and *n*-heptane. Similar to CRMM, the VOC profiles for NGCI's fugitive emissions are entirely different from its stack emissions. High contributions of propane were detected at two fugitive emission points, along with MTBE, styrene, formaldehyde, and acetone.

In contrast, AM shows similar VOC profiles for both stack and fugitive emissions, likely because the AM cluster is situated farther from other industry clusters, resulting in minimal external interference. VOC

emissions in AM primarily stem from the use of VOC-containing solvents, with alkanes and aromatics such as cyclohexane, 2,3-dimethylpentane, *iso*-pentane, ethylbenzene, and *m/p*-xylene being the main detected species.

3.3. Inhalation carcinogenic and non-carcinogenic risks

The chronic health risks associated with exposure to 47 toxic VOCs were assessed. For non-carcinogenic risks, an HQ value above 1 indicates potential non-carcinogenic health risks, while values between 0.1 and 1 suggest possible health concerns. The results showed that among the 38 toxic VOCs (non-carcinogenic risk), acrolein (14.96 ± 33.58), benzyl chloride (5.93 ± 36.57), trichloroethylene (1.66 ± 3.33), and 1,1,2-trichloroethane (1.04 ± 4.26) had HQ values greater than 1 (Fig. 4). These four species, although accounting for only $3.24 \pm 2.97\%$ of the H-VOCs by mixing ratio, contributed $94.93 \pm 4.95\%$ of the HI. Despite their relatively low volume fraction, long-term inhalation

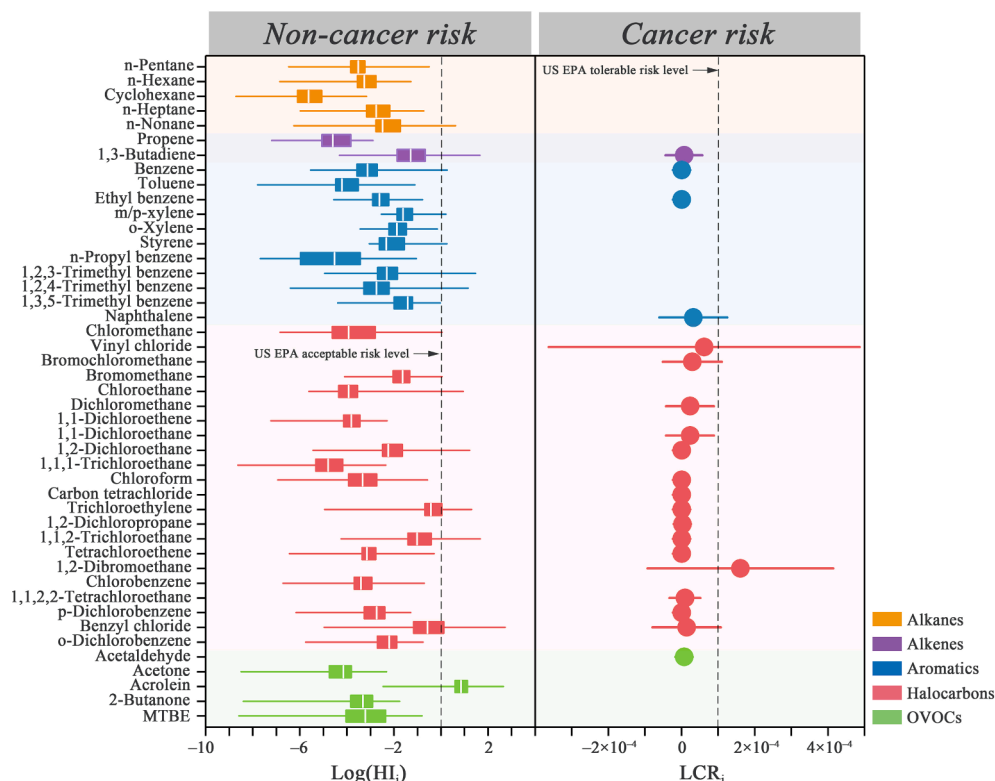


Fig. 4. Inhalation non-carcinogenic and carcinogenic risks of 46 H-VOCs in industrial parks.

exposure to these VOCs could pose significant chronic non-carcinogenic health risks to residents in the industrial park. The VOCs with HQs between 0.1 and 1, such as 1,3-butadiene (0.63 ± 3.26), 1,2-dichloroethane (0.21 ± 1.48), and 1,2,3-trimethyl benzene (0.14 ± 1.84), should also be given attention.

According to the classifications by the IARC, VOC species with an LCR greater than 10^{-4} , between 10^{-4} and 10^{-6} , and less than 10^{-6} could be categorized as confirmed risks, potential risks, and negligible risks, respectively (Li et al., 2023; Xiong et al., 2022). Among the 20 evaluated carcinogenic VOC species, 1,2-dibromoethane ($1.61 \times 10^{-4} \pm 2.54 \times 10^{-4}$) had an LCR exceeding 10^{-4} , indicating a definitive carcinogenic risk and necessitating special attention. Although 1,2-dibromoethane accounts for only 2.39 ± 1.74 % of the H-VOCs by mixing ratio, it contributed 54.45 ± 21.43 % of the HI. The vinyl chloride ($6.18 \times 10^{-5} \pm 4.25 \times 10^{-4}$), naphthalene ($3.23 \times 10^{-5} \pm 9.32 \times 10^{-5}$), bromochloroethane ($2.94 \times 10^{-5} \pm 8.14 \times 10^{-5}$), dichloromethane ($2.33 \times 10^{-5} \pm 6.61 \times 10^{-5}$), 1,1-dichloroethane ($2.33 \times 10^{-5} \pm 8.34 \times 10^{-5}$), benzyl chloride ($1.41 \times 10^{-5} \pm 9.36 \times 10^{-5}$), 1,1,2,2-tetrachloroethane ($9.36 \times 10^{-6} \pm 4.29 \times 10^{-5}$), acetaldehyde ($7.3 \times 10^{-6} \pm 2.15 \times 10^{-5}$), 1,3-butadiene ($6.66 \times 10^{-6} \pm 5.09 \times 10^{-5}$), and 1,2-dichloropropane ($2.55 \times 10^{-6} \pm 7.28 \times 10^{-6}$) had LCR values above 10^{-6} (Fig. 4). These compounds also pose potential risks that should not be overlooked. Overall, the cumulative inhalation risk of VOCs is significant, with HI and total LCR of 24.67 ± 60.24 and $2.85 \times 10^{-4} \pm 5.93 \times 10^{-4}$, respectively, exceeding the acceptable risk levels by the US EPA.

To investigate the carcinogenic and non-carcinogenic risks of inhaling H-VOCs by workers in different industrial clusters of the industrial park, the health risk levels based on offline monitoring datasets were assessed. The HI ranked as follows: CRMM (255.52 ± 136.03) > NGCI (227.74 ± 87.93) > PMI (214.85 ± 60.49) > ISI (169.01 ± 54.52) > AM (141.58 ± 48.3), and the total LCR from highest to lowest was ISI ($7.8 \times 10^{-3} \pm 5.23 \times 10^{-3}$) > PMI ($2.17 \times 10^{-3} \pm 1.29 \times 10^{-3}$) > CRMM ($2.02 \times 10^{-3} \pm 1.35 \times 10^{-3}$) > NGCI ($1.72 \times 10^{-3} \pm 1.21 \times 10^{-3}$) > AM ($6.36 \times 10^{-4} \pm 4.94 \times 10^{-4}$). The residential area (RA) had an HI of 52.46 ± 26.02 and a total LCR of $1.24 \times 10^{-3} \pm 9.94 \times 10^{-4}$. The HI in the residential area was significantly lower than in the five industrial sectors. However, the non-carcinogenic risk levels in these sectors were two to five times higher than in the residential area (Fig. 5). The total LCR in the residential area was higher than in AM but lower than in the other four sectors. The carcinogenic risk level in the ISI sector was approximately six times higher than in the residential area. At the species level, acrolein accounted for the majority of the HI in the ambient air of the five industrial clusters, with contribution rates

ranging from 84.56 % to 97.92 %. Moreover, certain VOC species with HI values greater than 1 in each industrial sector warrant attention, such as benzene and butadiene in ISI, 1,2-dichlorobenzene and chloromethane in CRMM, and 1,2-dichloroethane in NGCI and PMI. The primary carcinogens in the ambient air of the five industrial clusters were 1,2-dibromoethane, benzene, and carbon tetrachloride, with a cumulative LCR contribution rate exceeding 50 %. The workers in various industrial clusters may face more severe potential health risks, emphasizing the necessity of implementing control measures to reduce the exposure of H-VOCs.

3.4. O-VOC odor activity assessment

The odor intensity of individual target species among O-VOCs is mainly determined by their chemical concentration and detection threshold. To identify the main odor-causing substances within the industrial park, the olfactory effects of 52 O-VOCs were calculated based on these parameters (Fig. S2). The average values for OAV_{sum} and OAV_{max} in the industrial park were 1.03 ± 1.48 and 0.83 ± 2.71 , respectively. An OAV exceeding 1 is generally considered to cause perceptible odor nuisance, indicating a significant odor pollution risk (Sun et al., 2023; Xue et al., 2022). The top three compounds in terms of OAV were *p*-diethyl benzene, isopropyl benzene, and *p*-ethyl toluene, with OAVs of 0.62 ± 1.03 , 0.22 ± 2.6 , and 0.16 ± 1.21 , respectively. The remaining species had OAV values that did not exceed 0.01. Together, these three compounds constituted only 0.85 ± 1.41 % of TVOCs but contributed 72.89 ± 28.24 % to the OAV_{sum} . Theoretically, without synergistic effects among different O-VOC species, the odor intensity depends on the OAV_{max} (Blazy et al., 2014; Zahn et al., 2021). However, in the presence of synergistic effects, species with high OAV values also play a crucial role in the cumulative odor impact (OAV_{sum}). Therefore, odor mitigation efforts should focus on compounds with high OAV values.

Based on offline monitoring in five industrial clusters within the industrial park, the OAV_{sum} and OAV_{max} values, ranked from highest to lowest, followed the pattern of PMI (0.54 ± 0.23 , 0.24 ± 0.16) > CRMM (0.5 ± 0.36 , 0.19 ± 0.14) > NGCI (0.4 ± 0.29 , 0.16 ± 0.12) > ISI (0.38 ± 0.16 , 0.12 ± 0.03) > AM (0.31 ± 0.13 , 0.11 ± 0.06). Concurrently, the RA showed OAV_{sum} and OAV_{max} values of 0.28 ± 0.07 and 0.13 ± 0.06 , respectively, with the RA's OAV_{sum} being lower than that of all five industrial clusters. Yet, its OAV_{max} was higher than that of AM (Fig. 5). Acrolein was the predominant O-VOC across the industrial clusters, except for in the NGCI, significantly influencing the OAV_{sum} and overall

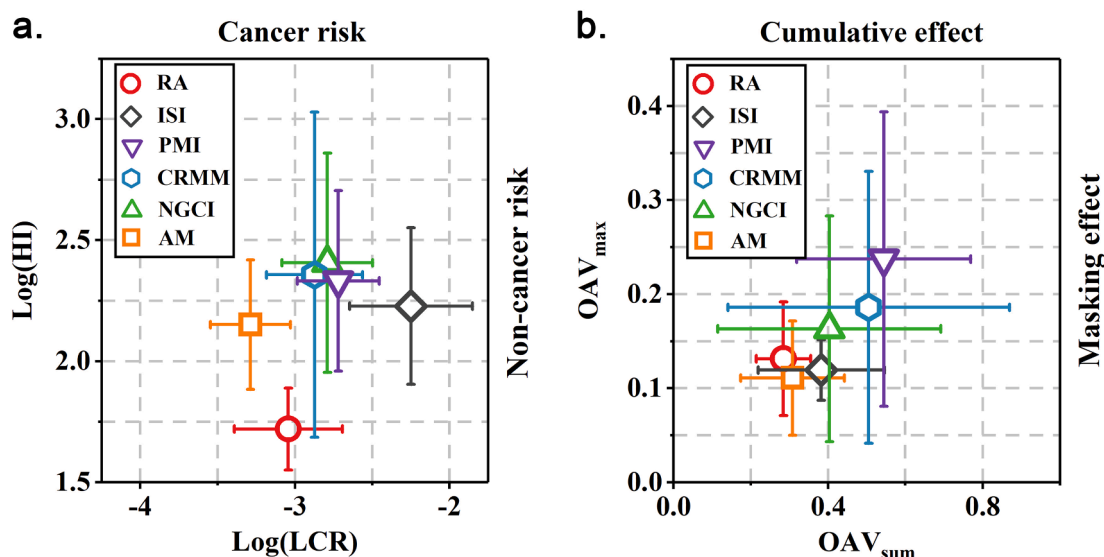


Fig. 5. Health risks and odor pollution levels in residential areas and five industrial clusters in the industrial park.

odor pollution in the industrial park. Furthermore, *p*-diethyl benzene notably contributed to the OAV_{sum} in the NGCI, CRMM, and AM. Beyond these common compounds, characteristic species in different industrial clusters also showed high OAV values, such as *p*-ethyl toluene, *n*-propyl benzene, and toluene in NGCI, ethanol in CRMM, toluene in PMI, styrene in ISI, and *p*-xylene in AM.

3.5. Risk-oriented source apportionment

3.5.1. Identification of significant emission sources

The PMF model was used to identify the source profiles of H-VOCs and O-VOCs in the ambient air of the industrial park. The source apportionment results are provided in Text S3. The optimal outcomes of the PMF-derived factors were matched by integrating the actual distribution of pollution sources in the industrial park with the real-time monitoring data of key pollutant VOC source profiles. The H-VOCs and O-VOCs predominantly originate from six sources, ranked by contribution as follows: IST (32.59 %), NGCI (27.77 %), diesel vehicle exhaust (DVE, 12.04 %), PMI (11.14 %), CRMM (9.96 %), and ISI (6.5 %). The six major sources identified by the PMF analysis align with the distribution characteristics of nearby pollution emission sources. Within a 3-km radius of the observation site, multiple polluting enterprises are situated, including industries such as NGCI, PMI, and CRMM, with the NGCI cluster being larger and closer to the monitoring site. Almost every enterprise within these industries involves IST, which is likely a major factor contributing to its highest rate. The ISI cluster, located approximately 8 km southeast of the observation site, contributes less due to its relatively distant location.

3.5.2. Pmf-resolved vs. Measured source profiles of stationary sources

In the industrial park, various stationary sources are involved in numerous emission segments, such as stack and fugitive emissions from

various production lines and workshops. To more precisely identify the importance of each emission segment within each source category to the atmospheric H-VOCs and O-VOCs, a multiple linear regression model was used to assess the emission segments of each source category. The VOC emission segments involved in each source category, along with their impact on the PMF-derived source profiles, are listed in Table S7.

Iron and steel industry. The VOC source profile measured for the ISI included three stack emission points (coking, sintering, and iron smelting) and three fugitive emission points (coal charging, coal refining, and factory center boundary). The multiple linear regression model results indicated that the coking, iron smelting, and coal refining variables were included, while sintering, coal charging, and the factory center boundary were excluded. The three retained independent variables collectively explained 49.8 % of the dependent variable (PMF source profile), with the source profiles from coking, iron smelting, and coal refining explaining 39.4 %, 4.4 %, and 7.9 % of the PMF source profile, respectively. Compared with other sources, the source profile measured for the ISI explained a relatively lower proportion of the PMF source profile, potentially due to the greater distance of the ISI cluster from the observation site and significant changes in the composition of the main VOC reactive species during atmospheric transport. The reconstructed source profile showed high consistency with the PMF source profile ($r = 0.75$), especially for typical high mixing ratio species in the steel industry, such as toluene, ethane, benzene, meta/*para*-xylene, and acetone (Fig. 6a). CBPF plots indicated that at higher wind speeds (>2 m/s), the source transport from the steel manufacturing site was likely (>0.5 CPF) from the northeast direction, consistent with the actual location of the ISI cluster in the industrial park (Fig. S3). Under low wind conditions (<2 m/s), the range of high CPF values was broader, likely due to greater lateral dispersion of air pollutants at lower wind speeds.

Pharmaceutical manufacturing industry. The stack emissions from

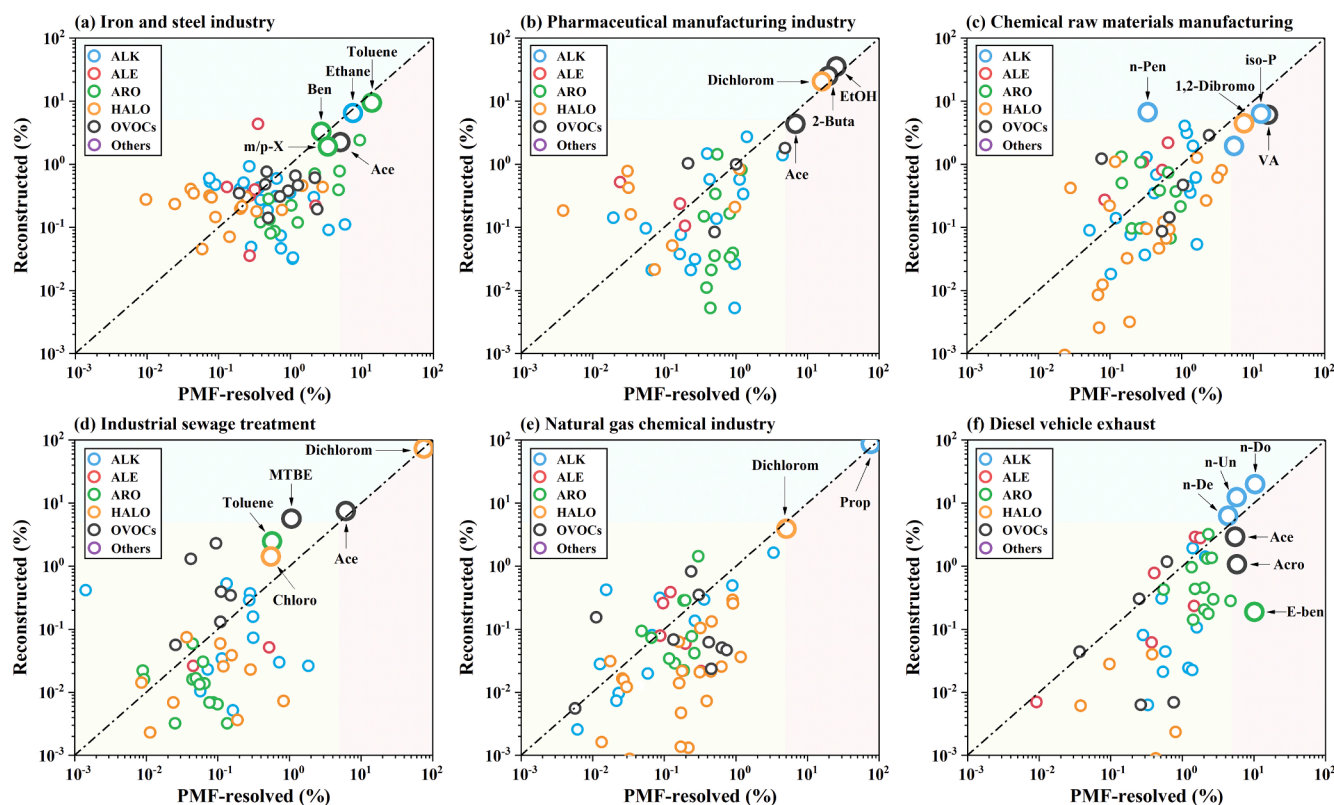


Fig. 6. Comparison of the source profiles of PMF-resolved and emission source reconstructed. The VOC species in the light red and light blue areas indicate a contribution of $>5\%$. The abbreviations for VOC species are summarized in Table S8. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

chemical synthesis pharmaceutical processes predominantly influence the PMF source profile for the PMI. The source profiles from emissions outlets #1 and #2 in the chemical synthesis pharmaceutical workshop accounted for 86 % and 9 % of the PMF source profile, respectively, cumulatively explaining 95 % of the total. The correlation coefficient between the reconstructed source profile and the PMF source profile is as high as 0.98, with closely matched mixing ratios of high-density species, such as ethanol, 2-butanone, dichloromethane, and acetone (Fig. 6b). Regarding the direction of pollutant transport, the PMI sources primarily originate from the low wind speed areas to the southwest of the observation site. The direction of pollution sources aligns closely with the actual location of the PMI cluster in the industrial park, and the PMI cluster is located near the observation site.

Chemical raw materials manufacturing. The fit between the measured source profiles and the PMF-resolved source profile for the CRMM is relatively poor. The four variables used in the model (two production workshop vents, workshop fugitive emissions, and the plant boundary center) cumulatively explain only 32.4 % of the PMF-resolved source profile, and the correlation coefficient ($r = 0.69$) between the reconstructed source profile and the PMF-resolved source profile is significantly lower than in other industries. The diversity of enterprises in the CRMM cluster within the industrial park, along with vastly different production processes for various chemical materials, results in the measured source profiles having relatively low representativeness for this industry. The source distribution of the CRMM, similar to the ISI as observed in the CPF results, is widespread, primarily because both the CRMM and ISI clusters are located southeast of the observation site (Fig. 1). In addition, the numerous transmission channels for CRMM are a major reason for the low explanation rate of the measured source profiles for the PMF-resolved source profile.

Industrial sewage treatment. The measured source profiles for IST originate from the emissions captured at the exhaust outlets of sewage treatment facilities within the PMI, NGCI, and CRMM. Regression model outcomes indicate that the source profile of IST is predominantly influenced by the emissions from PMI's sewage treatment. The source profile from PMI explains 98.5 % of the PMF-resolved source profile, while the contribution from NGCI and CRMM sewage treatments is less than 1 %. The CBPF diagram for IST corroborates this finding, showing a transmission direction from IST that aligns closely with the PMI.

Natural gas chemical industry. Fugitive emissions from chemical product production lines predominantly influence the PMF source profile for the NGCI. VOC components measured from these lines explain 91.6 % of the PMF-resolved source profile. In comparison, other

collected source profiles from exhaust outlets and fugitive sources do not exceed 1 %, despite these source profiles containing the same major VOC species (propane) as the PMF-resolved source profile. CBPF results indicate that sources from the NGCI mainly originate from the southwest direction ($CPF > 0.5$) at low wind speeds, and the direction of pollutant transport aligns with the location of the NGCI cluster.

3.5.3. Identification and quantification of risk sources

The contributions of six categories to health risks and odor pollution were quantitatively assessed based on the source apportionment results (Fig. 7). NGCI (9.16 ± 11.89), IST (8.47 ± 9.23), and CRMM (6.9 ± 6.4) exhibited the highest non-carcinogenic risks, significantly surpassing those from ISI (1.95 ± 1.41), DVE (1.89 ± 1.67), and PMI (0.14 ± 0.17). The spatial distribution of HI contributions from the CPF analysis also supports this finding, with significant contributions oriented toward the southwest where the NGCI and PMI clusters are located (Fig. 8a). The high HI values in the PMI cluster are primarily contributed by its sewage treatment phase, aligning with the conclusions of section 3.5.2. CRMM exhibited the highest carcinogenic risk (LCR of $1.11 \times 10^{-4} \pm 1.08 \times 10^{-4}$), followed by IST ($7.88 \times 10^{-5} \pm 9.25 \times 10^{-5}$), NGCI ($7.2 \times 10^{-5} \pm 6.61 \times 10^{-5}$), DVE ($6.55 \times 10^{-5} \pm 4.46 \times 10^{-5}$), ISI ($5.48 \times 10^{-5} \pm 5.45 \times 10^{-5}$), and PMI ($1.45 \times 10^{-5} \pm 1.17 \times 10^{-5}$). The CPF distribution of LCR is similar to that of CRMM, with CPF high-value points for LCR being more widespread than those for HI (Fig. 8b). The species posing the most significant health risks are similar across sources. However, the specific high-risk benchmark species vary somewhat between industries. Specifically, acrolein was the predominant species contributing to the non-carcinogenic risk in ISI, CRMM, IST, and DVE, with contribution rates of 92.99 ± 8.06 %, 87.33 ± 11.25 %, 51.62 ± 22.51 %, and 67.96 ± 18.23 %, respectively. For PMI and NGCI, the primary non-carcinogenic risk species were 1,1,2-trichloroethane and 2-chlorotoluene, contributing 31.1 ± 23.06 % and 45.14 ± 20.01 %, respectively. Similarly, 1,2-dibromoethane was the leading carcinogenic risk species for PMI, CRMM, NGCI, and DVE, with contribution rates of 51.8 ± 28.79 %, 57.8 ± 23.69 %, 29.78 ± 25 %, and 84.23 ± 22.6 %, respectively. In the ISI and IST, naphthalene and dichloromethane were the top contributors to the non-carcinogenic risk, with contribution rates of 44.69 ± 22.21 % and 28.14 ± 15.46 %, respectively.

The contributions of the six sources to OAV_{sum} and OAV_{max} are consistent in the order of DVE, ISI, CRMM, PMI, IST, and NGCI (Fig. 7b). DVE significantly contributes more to OAV than the other sources, with OAV_{sum} and OAV_{max} values of 0.65 ± 0.76 and 0.42 ± 0.44 , respectively. The CPF high-value points for OAV_{sum} are widespread, possibly

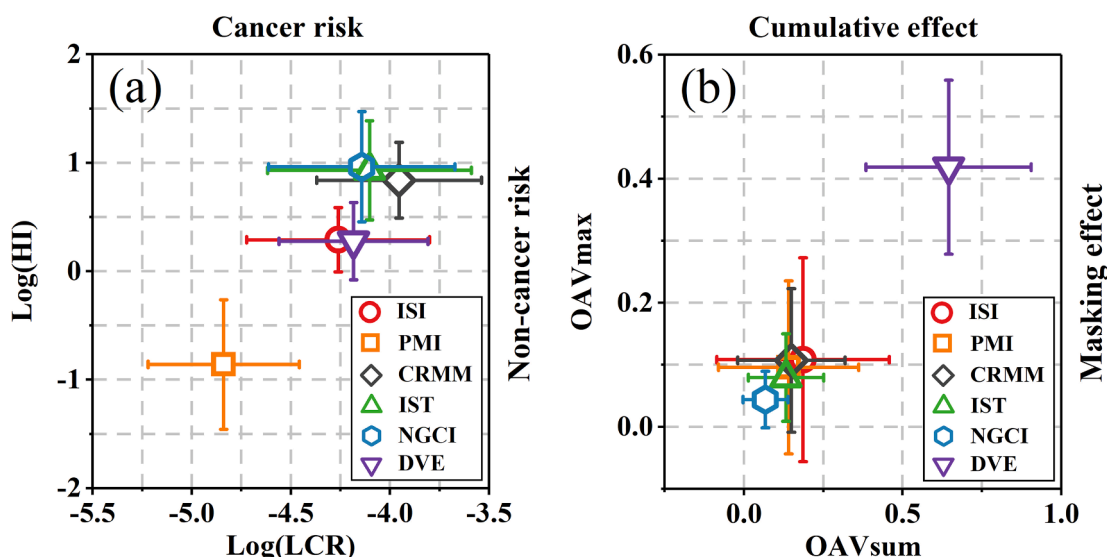


Fig. 7. Health risks and odor pollution levels from six major sources in the industrial park.

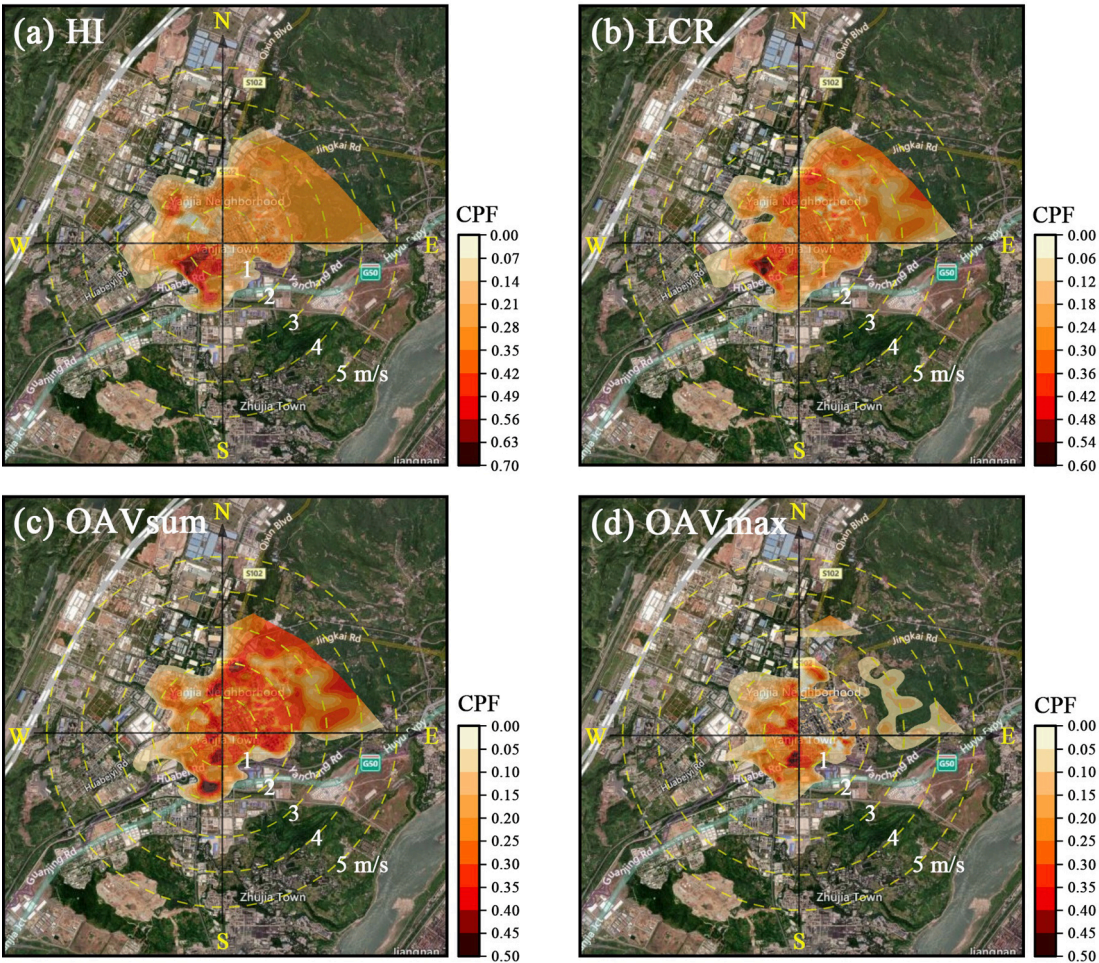


Fig. 8. Spatial distribution of CPF for health risks and odor pollution in the industrial park.

due to the ubiquitous presence of diesel vehicle cargo transport throughout the entire industrial park (Fig. 8c). By contrast, the CPF high-value points for OAV_{max} are primarily concentrated in low-wind areas on the west and south sides. This could be due to their proximity to main traffic arteries where diesel vehicles are more densely

distributed and the exhaust emissions are higher (Fig. 8d). In terms of specific VOC species contributing to OAV, benzene derivatives and OVOCs, such as *p*-xylene, isopropyl benzene, *n*-propyl benzene, *p*-diethyl benzene, methacrolein, and acrolein, are predominant across sources. Specifically, the dominant OAV species for PMI, CRMM, NGCI,

Table 1
Key VOC-controlled species and their emission reduction shares from six major sources in the industrial park.

Control species	Total	ISI	PMI	CRMM	IST	NGCI	DVE	Control indicators
		Reduction rate (%)						
n-Nonane	30.81	2.95		3.28	8.41		16.18	HI
1,3-Butadiene	70.67	1.66	4.25	5.61	45.60	4.76	8.78	HI/LCR/OAV
Benzene	18.69	18.39			0.30			HI/LCR/OAV
<i>m/p</i> -Xylene	5.36	0.33	0.56	0.82	0.25	0.32	3.08	HI/OAV
Styrene	24.69		2.58	3.32	0.82	4.25	13.71	HI/OAV
<i>iso</i> -Propyl benzene	76.45	8.40	16.68	8.78	5.50	2.29	34.80	OAV
<i>p</i> -Ethyl toluene	79.02	8.41	15.80	5.16	5.49		44.15	OAV
1,2,3-Trimethyl benzene	78.16	13.68	8.11	9.12	2.99		44.27	HI
1,2,4-Trimethyl benzene	78.45	9.90	12.39	7.48	2.35		46.32	HI/OAV
<i>p</i> -Diethyl benzene	35.12	2.16	3.66	5.38	1.62	2.12	20.17	OAV
Naphthalene	14.66	10.20		1.62	0.86	1.22	0.76	LCR
Chloromethane	4.11		1.65		0.16	2.31		HI
Dichloromethane	8.36		0.52	0.13	7.29	0.42		LCR/OAV
1,2-Dichloroethane	73.87	1.84		1.34	18.68	52.02		LCR
Trichloroethylene	68.73	0.24		18.04	22.14	20.54	7.78	HI/LCR/OAV
1,1,2-Trichloroethane	73.01	4.59	2.94	6.00	5.89	53.55	0.04	LCR
1,2-Dibromoethane	22.48	2.04	1.01	8.23	0.68	2.80	7.73	LCR
2-Chlorotoluene	92.87			1.67	36.10	55.10		HI/LCR
Acrolein	93.75	14.51		31.92	22.77	17.75	6.79	HI/OAV
Methacrolein	20.36	2.65		3.41	4.91	6.52	2.88	OAV

and DVE were *p*-diethyl benzene, with contribution rates of $43.9 \pm 33.73\%$, $61.61 \pm 34.07\%$, $53.88 \pm 32.76\%$, and $53.31 \pm 33.04\%$, respectively. In contrast, the primary OAV species for ISI and IST were *n*-propyl benzene and methacrolein, with contribution rates of $35.92 \pm 17.73\%$ and $39.38 \pm 28.37\%$, respectively.

3.6. Policy implications

To ensure the residents and workers in the industrial park are not exposed to health risks and odor nuisances, the IMTs and reduction rates for 20 VOC species that frequently exceed their respective risk thresholds daily were calculated. Table 1 shows the total reduction rates for these VOCs and the contribution to reductions from six major sources. The highest reduction rates were acrolein and chlorobenzene, reaching 93.75 % and 92.87 %, respectively. These were followed by *p*-diethyl benzene (79.02 %), 1,2,4-trimethyl benzene (78.45 %), 1,2,3-trimethyl benzene (78.16 %), isopropyl benzene (76.45 %), 1,2-dichloroethane (73.87 %), 1,1,2-trichloroethane (73.01 %), 1,3-butadiene (70.67 %), and trichloroethylene (68.73 %), with lower reduction rates for the remaining species.

Each target species for reduction varies within the industrial park considering the emission reduction shares from different sources. Specifically, ISI should focus on reducing aromatic compounds, such as benzene, 1,2,3-trimethyl benzene, naphthalene, and acrolein, mainly through targeted control measures in coking processes. The PMI should prioritize controlling isopropyl benzene, *p*-ethyl toluene, and 1,2,4-trimethyl benzene, with stack emissions of VOCs from chemical synthesis workshops as a primary control target. CRMM has shared in reducing various VOCs, among which the effective reduction of trichloroethylene and benzyl chloride is particularly important. IST is also a significant source of VOC emissions that cannot be ignored, contributing significantly to VOC sources at the observation site and holding higher reduction rates for species such as 1,3-butadiene, dichloromethane, 1,2-dichloroethane, trichloroethylene, benzyl chloride, and acrolein. Therefore, enterprises in sewage treatment within the industrial park should focus on VOC emissions from this process, especially in PMI. NGCI has taken on most of the reduction for 1,2-dichloroethane, 1,1,2-trichloroethane, and benzyl chloride, with the reduction rates for these species exceeding 50 % of the total reduction. The control of fugitive emissions of VOCs in the production lines of chemical products is particularly crucial in this sector. Isopropyl benzene, *p*-diethyl benzene, 1,2,3-trimethyl benzene, and 1,2,4-trimethyl benzene are the target species for DVE, but control of mobile sources compared with stationary sources is more challenging and requires stricter and more personalized measures. In summary, effectively controlling key VOC emission processes and reducing target species in the industrial park can lead to significant environmental and health benefits for local residents and workers.

Based on the quantitative identification of risk levels from different VOC sources in industrial parks and the IMT analysis, results and considering common issues present in industrial parks nationwide, it is crucial from a health risk management perspective to emphasize the following points in the formulation of VOC control policies for industrial parks. (1) Given the high risk and multiple sources of VOC emissions from IST, it is necessary to establish corresponding emission standards to limit the concentration of high-risk VOC species. (2) Due to the significant contribution of heavy-duty DVE to pathogenicity and odor, efforts should be accelerated to enhance fuel standards and promote the use of alternative energy sources. This includes limiting the content of benzene compounds in fuels and strategically planning transportation routes to avoid residential areas. (3) Within the policy framework, priority should be given to reducing high-risk VOC species (e.g., acrolein, 1,2-dibromoethane, and 2-chlorotoluene), not just focusing on the total emission of VOCs within permissible limits. This includes setting stricter emission limits for these species and strengthening monitoring and enforcement. (4) Risk warnings should be issued for high-risk species, and timely risk

alerts should be provided to the public to reduce exposure risks for residents and workers.

3.7. Uncertainty and sensitivity analysis

The Monte Carlo simulation method was used to assess these risk sources quantitatively and to analyze the uncertainties and sensitivities in the health risks and odor pollution posed by various VOC sources. The uncertainty in risk sources encompasses three aspects of uncertainty transmission: (1) VOC species monitoring concentrations (C_i), (2) parameters used in the risk assessment process, and (3) factor profiles (FP_i) resolved by the PMF model. The uncertainty results for each risk source in terms of health risks and odor pollution at a 95 % confidence level are presented in Table S9. Sensitivity analysis indicates that FP_i significantly contributes to the total variation in HI for all six categories of risk sources. $FP_{Acrolein}$ accounted for the majority of the total HI variation in ISI, CRMM, IST, and DVE, whereas $FP_{1,1,2-Trichloroethane}$ and $FP_{Benzyl\ chloride}$ were the primary sensitive factors for PMI and NGCI, respectively. Multiple sensitivity factors are involved in the six carcinogenic risk sources, and none significantly contribute to the total variation in LCR. FP and EF are significant sensitive factors for the six carcinogenic risk sources. For OAV, *p*-diethyl benzene, isopropyl benzene, and methacrolein are key species affecting the sensitivity of the six categories of odor risk sources, with their concentrations, FP , and OT significantly contributing to the total variation in OAV.

This study emphasized the impact of exposure to H-VOCs and O-VOCs on health and odor risks in an industrial park. However, other pollutants, such as alcohols, esters, polycyclic aromatics, amines, and particulate matter, can also pose risks. Therefore, the overall risk from the six sources in the industrial park may be higher than the estimation. Further study on a broader range of pollutants is needed and would be interesting and fruitful.

4. Conclusions

This study provides a combined measurement from high-resolution observations and offline datasets of VOCs. The one-year online observations of the industrial park revealed that the inhalation health risk of VOCs is high. The HI and LCR were 24.67 ± 60.24 and $2.85 \times 10^{-4} \pm 5.93 \times 10^{-4}$, respectively. Both exceed the acceptable risk levels of the US EPA. The risk for workers in specific sectors is two to six times higher than that for residents. PMF identified six primary risk sources and their significant emission processes within the industrial park. The assessment of these six risk sources showed that the NGCI (HI: 9.16 ± 11.89) posed the highest non-carcinogenic risks, CRMM (LCR: $1.11 \times 10^{-4} \pm 1.08 \times 10^{-4}$) presented the highest carcinogenic risks, and DVE (OAV_{max}: 0.65 ± 0.76) contributed most significantly to odor pollution. Twenty high-risk VOC species were identified that require reduction, with reduction rates ranging from 4.11 % to 93.75 %. The targeted reduction of VOC species from these six major sources and effective control of significant VOC emission processes can yield substantial environmental and health benefits for local residents and workers.

CRedit authorship contribution statement

Ling Li: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation. **Fengwen Wang:** Writing – review & editing, Writing – original draft, Formal analysis, Conceptualization. **Wei Hu:** Visualization, Software, Investigation, Data curation. **Dan Zhang:** Writing – original draft, Project administration, Methodology, Funding acquisition, Conceptualization. **Zhenliang Li:** Software, Methodology, Data curation. **Pingjiang Lv:** Software, Investigation. **Qin Xu:** Data curation. **Rui Yuan:** Investigation. **Yunhuai Zhang:** Writing – review & editing. **Yong Zhang:** Writing – review & editing. **Hai Guo:** 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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envint.2024.109137>.

Data availability

Data will be made available on request.

References

- Blazy, V., Guardia, A.D., Benoist, J.C., Daumoin, M., Lemasle, M., Wolbert, D., et al., 2014. Odorous gaseous emissions as influence by process condition for the forced aeration composting of pig slaughterhouse sludge. *Waste. Manage.* 34, 1125–1138.
- Chai, F., Li, P., Li, L., Qiu, Z., Han, Y., Yang, K., 2022. Dispersion, olfactory effect, and health risks of VOCs and odors in a rural domestic waste transfer station. *Environ. Res.* 209, 112879.
- Chen, Q., Sun, H., Zhang, J.Y., Xu, Y., Ding, Z., 2019. The hematologic effects of BTEX exposure among elderly residents in Nanjing: a cross-sectional study. *Environ. Sci. Pollut. Res.* 26, 10552–10561.
- Cheng, Z., Sun, Z., Zhu, S., Lou, Z., Zhu, N., Feng, L., et al., 2019. The identification and health risk assessment of odor emissions from waste landfilling and composting. *Sci. Total Environ.* 649, 1038–1044.
- Cheng, L., Wei, W., Guo, A., Zhang, C., Sha, K., Wang, R., et al., 2022. Health risk assessment of hazardous VOCs and its associations with exposure duration and protection measures for coking industry workers. *J. Clean. Prod.* 397, 134919.
- Du, Z.J., Mo, J.H., Zhang, Y.P., 2014. Risk assessment of population inhalation exposure to volatile organic compounds and carbonyls in urban China. *Environ. Int.* 73, 33–45.
- Duan, Z., Lu, W., Mustafa, M.F., 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.
- Gao, Z., Hu, G., Wang, H., Zhu, B., 2019. Characterization and assessment of volatile organic compounds (VOCs) emissions from the typical food manufactures in Jiangsu province. *China. Atmos. Pollut. Res.* 10, 571–579.
- Han, B., Liu, Y., Wu, J., Feng, Y., 2018. Characterization of industrial odor sources in Binhai New Area of Tianjin. *China. Environ. Sci. Pollut. Res.* 25, 14006–14017.
- Hsu, C., Wu, P., Chen, Y., Chen, P., Guo, Y.L., Lin, Y., et al., 2022. An integrated strategy by using long-term monitoring data to identify volatile organic compounds of high concern near petrochemical industrial parks. *Sci. Total Environ.* 821, 153345.
- Hu, R., Liu, G., Zhang, H., Xue, H., Wang, X., 2018. Levels, characteristics and health risk assessment of VOCs in different functional zones of Hefei. *Ecotox. Environ. Safe.* 160, 301–307.
- Hu, R., Liu, G., Zhang, H., Xue, H., Wang, X., Lam, P.K.S., 2020. Odor pollution due to industrial emission of volatile organic compounds: A case study in Hefei. *China. J. Clean. Prod.* 246, 119075.
- Jia, H., Gao, S., Duan, Y., Fu, Q., Che, X., Xu, H., et al., 2021. Investigation of health risk assessment and odor pollution of volatile organic compounds from industrial activities in the Yangtze River Delta region. *China. Ecotox. Environ. Safe.* 208, 111474.
- Li, Y., Yin, S., Yu, S., Yuan, M., Dong, Z., Zhang, D., et al., 2020. Characteristics, source apportionment and health risks of ambient VOCs during high ozone period at an urban site in central plain. *China. Chemosphere.* 250, 126283.
- Li, M., Zhang, Q., Zheng, B., Tong, D., Lei, Y., Liu, F., et al., 2019. Persistent growth of anthropogenic non-methane volatile organic compound (NMVOC) emissions in China during 1990–2017: drivers, speciation and ozone formation potential. *Atmos. Chem. Phys.* 19, 8897–8913.
- Li, L., Zhang, D., Hu, W., Yang, Y., Zhang, S., Yuan, R., et al., 2023. Improving VOC control strategies in industrial parks based on emission behavior, environmental effects, and health risks: A case study through atmospheric measurement and emission inventory. *Sci. Total Environ.* 865, 161235.
- Lin, Q., Gao, Z., Zhu, W., Chen, J., An, T., 2023. Underestimated contribution of fugitive emission to VOCs in pharmaceutical industry based on pollution characteristics, odorous activity and health risk assessment. *J. Environ. Sci.* 126, 722–733.
- Liu, Y., Lu, W., Wang, H., Gao, X., Huang, Q., 2019. Improved impact assessment of odorous compounds from landfills using Monte Carlo simulation. *Sci. Total Environ.* 648, 805–810.
- Lu, W., Duan, Z., Li, D., Luis, M.C.J., Liu, Y., Guo, G., et al., 2015. Characterization of odor emission on the working face of landfill and establishing of odorous compounds index. *Waste. Manage.* 42, 74–81.
- Pitiriciu, M., Tansel, B., 2021. Volatile organic contaminants (VOCs) emitted from sewer networks during wastewater collection and transport. *J. Environ. Manage.* 285, 112136.
- Rana, L., Dahlberg, S., Steinmaus, C., Zhang, L.P., 2021. Benzene exposure and non-Hodgkin lymphoma: a systematic review and meta-analysis of human studies. *Lancet. Planet. Health.* 5, 633–643.
- Simayi, M., Hao, Y., Li, J., Wu, R., Shi, Y., Xi, Z., 2019. Establishment of county-level emission inventory for industrial NMVOCs in China and spatial-temporal characteristics for 2010–2016. *Atmos. Environ.* 211, 194–203.
- Song, M., Li, X., Yang, S., Yu, X., Zhou, S., Yang, Y., et al., 2021. Spatiotemporal variation, sources, and secondary transformation potential of volatile organic compounds in Xi'an. *China. Atmos. Chem. Phys.* 21, 4939–4958.
- Sun, C., Wang, Z., Yang, Y., Wang, M., Jing, X., et al., 2023. Characteristics, secondary transformation and odor activity evaluation of VOCs emitted from municipal solid waste incineration power plant. *J. Environ. Manage.* 138, 116–124.
- Wu, R., Bo, Y., Li, J., Li, L., Li, Y., Xie, S., 2016. Method to establish the emission inventory of anthropogenic volatile organic compounds in China and its application in the period 2008–2012. *Atmos. Environ.* 127, 244–254.
- Xiong, Y., Bari, M.A., 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.* 2020, 135970.
- Xiong, Y., Huang, Y., Du, K., 2022. Health risk-oriented source apportionment of hazardous volatile organic compounds in eight Canadian cities and implications for prioritizing mitigation strategies. *Environ. Sci. Technol.* 56, 12077–12085.
- Xue, S., Ding, W., Li, L., Ma, J., Chai, F., Liu, J., 2022. Emission, dispersion, and potential risk of volatile organic and odorous compounds in the exhaust gas from two sludge thermal drying processes. *Waste. Manage.* 138, 116–124.
- 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. *Ecotox. Environ. Safe.* 184, 109665.
- Zahn, J.A., Dispirito, Y.S., Do, Y.S., Brooks, B.E., Cooper, E.E., Hatfield, J.L., 2021. Correlation of human olfactory responses to airborne concentrations of malodorous Volatile Organic Compounds Emitted from Swine Effluent. *J. Environ. Qual.* 30, 624–634.
- Zarra, T., Galang, M.G., Ballesteros Jr., F., Belgioirno, V., Naddeo, V., 2019. Environmental odour management by artificial neural network – a review. *Environ. Int.* 133, 105189.
- Zhang, J., Xiao, J., Chen, X., Liang, X., Fan, L., Ye, D., 2018. Allowance and allocation of industrial volatile organic compounds emission in China for year 2020 and 2030. *J. Environ. Sci.* 69, 155–165.
- Zhou, J., You, Y., Bai, Z.P., Hu, Y.D., Zhang, J.F., Zhang, N., 2011. Health risk assessment of personal inhalation exposure to volatile organic compounds in Tianjin. *China. Sci. Total Environ.* 409, 452–459.