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Volatile organic compounds in an e-waste dismantling region: From spatial-seasonal variation to human health impact



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HIGHLIGHTS

- Ambient VOCs was studied in the ewaste dismantling region.
- BTEX in ambient air was found related with e-waste dismantling activity.
- The e-waste dismantling park is a hotspot of hazardous VOCs.
- The e-waste dismantling emission contributed 20% to total VOCs in adjacent ambient air.
- Higher inhalation health risks were found in the e-waste park than residential areas.

A R T I C L E I N F O

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GRAPHICAL ABSTRACT



ABSTRACT

The dismantling of electrical and electronic waste (e-waste) can release various Volatile organic compounds (VOCs), impacting the surrounding ambient environment. We investigated the spatio-temporal characteristics and health risks of the ambient VOCs emitted in a typical e-waste dismantling region by conducting multi-site sampling campaigns in four seasons. The pollution of benzene, toluene, ethylbenzene, and xylenes (BTEX) in the e-waste dismantling park has relation to e-waste dismantling by seasonal trend analysis. The highest concentrations of most VOCs occurred in winter and autumn, while the lowest levels were observed in summer and spring. The spatial distribution map revealed the e-waste dismantling park to be a hotspot of BTEX, 1,2-dichloropropane (1,2-DCP), and 1,2-dichloroethane (1,2-DCA), while two major residential areas were also the hotspots of BTEX. The e-waste emission source contributed 20.14% to the total VOCs in the e-waste dismantling park, while it was absent in the major residential and rural areas. The cancer risk assessment showed that six VOCs exceeded 1.0×10^{-6} in the e-waste dismantling park, while only three or four compounds exceeded this risk in other areas. The noncancer risks of all compounds were below the safety threshold. This study supplements the existing

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knowledge on VOC pollution from e-waste dismantling and expands the research scope of chemical pollution caused by e-waste.

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1. Introduction

Electrical and electronic waste (e-waste), the fastest-growing solid waste worldwide, is estimated to increase at an annual rate of 3%-5% globally (Cucchiella et al., 2015; Singh et al., 2016). In 2016, roughly 45 million tons of e-waste was generated worldwide (Baldé et al., 2017). In 2019, this figure increased to 54 million tons (Forti et al., 2020). The main end-of-life treatment options of ewaste include recycling, incineration, and landfill (Tsydenova and Bengtsson, 2011). E-waste contains many valuable resources such as noble metals and is therefore considered an attractive secondary source (Kaya, 2016). E-waste dismantling can yield several economic benefits (Zhang et al., 2019; Zhao et al., 2019). However, various contaminants, including organic pollutants and heavy metals, are released during the e-waste dismantling process, which may threaten the health of the environment and human beings (Huang et al., 2019; Li et al., 2008, 2020a). For example, a study reported that the atmospheric polychlorinated biphenyls (PCBs) of Vietnam were mainly released from uncontrolled discarded ewaste (Wang et al., 2016b). In southeastern China, high concentrations of heavy metal observed in a river in an e-waste dismantling town were attributed to e-waste recycling (Guo et al., 2009). In Australia, the soil around two formal e-waste recycling facilities was reported to be contaminated with polybrominated diphenyl ethers (PBDEs) and novel brominated flame retardants (NBFRs) originating from e-waste (McGrath et al., 2018).

Volatile organic compounds (VOCs) are one of the leading organic pollutants. They are ubiquitous pollutants affecting atmospheric chemistry and human health. The photochemical reactions and physical transformations of VOCs with oxides of nitrogen $(NO_x = NO + NO_2)$ could contribute to the formation of tropospheric ozone (Edwards et al., 2014) and particulate matter (Ji et al., 2020; Lu et al., 2019), causing severe air quality problems (Ma et al., 2016; Shao et al., 2016; Wu and Xie, 2017; Wu et al., 2017). Furthermore, exposure to VOCs can directly affect human health, causing respiratory diseases, neurological symptoms, and even cancers (Amor-Carro et al., 2020; Chen et al., 2002; Kampa and Castanas, 2008; Wang et al., 2016a). The Shanghai Health Study reported that benzene exposure resulted in an increased risk of various blood and bone marrow abnormalities (Gross and Paustenbach, 2018). Ambient VOCs from gasoline emissions, architectural paints, and household products are positively linked to increased emergency hospital admissions for chronic obstructive pulmonary disease (Ran et al., 2020). Hydrocarbons, particularly alkenes and alkynes, are associated with cardiovascular diseases, emergency department visits, while VOCs with ketone groups are associated with asthma emergency department visits (Ye et al., 2017). It was also reported that exposure to VOCs in e-waste dismantlers is associated with carcinogenic and non-carcinogenic risks (An et al., 2014b).

Several existing studies have quantified the emission of VOCs during the e-waste dismantling process (Alston et al., 2011; Guo et al., 2020). Among them, benzene, toluene, ethylbenzene, and xylene isomers (BTEX) are important VOC species as they can cause severe health effects (Miri et al., 2016). For example, the pyrolysis of e-waste releases large quantities of methane, ethene, benzene, and toluene (Alston et al., 2011). An et al. detected high concentrations

of aromatics in the rotary incinerator e-waste dismantling workshop, while equivalent amounts of aromatic and halogenated hydrocarbons were detected during the e-waste dismantling with electric heating furnaces (An et al., 2014b). These studies indicate that e-waste dismantling activity can lead to large-scale emission of VOCs. However, all these studies focused on the indoor dismantling process. Ambient VOC pollution due to the e-waste dismantling area has not been reported yet. The VOCs emitted from e-waste in rotary incinerators deserve urgent attention as they can pose cancer risk and noncancer risk to the exposed population (Chen et al., 2016). Since VOCs can easily diffuse from workshops to outdoors, it is crucial to study the outdoor VOCs pollution in the e-waste dismantling region.

In this study, we measured the ambient VOCs at multiple sites in four consecutive seasons in a small town famous for e-waste dismantling. This study aims to study the spatio-temporal variations of the VOCs in ambient air surrounding the e-waste dismantling area and its relationship with the dismantling activity. Factors considered in this study are: (1) the pollution profiles of main VOC species in the ambient air, (2) spatial and temporal characteristics of VOCs, (3) source identification and the source apportionment of ambient VOCs, (4) human cancer and noncancer risk assessment. This is the first study to comprehensively assess the ambient VOCs around the e-waste dismantling area, expanding the research scope of e-waste pollution.

2. Materials and method

2.1. Field sampling

Air samples were collected from an e-waste dismantling area during four grid-study campaigns in 2018 and 2019. The sampling was carried out on 28 December 2018 (11 °C-20 °C), 10 April 2019 (22 °C-31 °C), 16 July 2019 (28 °C-35 °C), and 31 October 2019 (21 °C-28 °C), representing the winter, spring, summer, and fall, respectively. Meteorological data were obtained from the meteorological information network of Guangdong province (Table S1) (https://www.gd121.cn/index.shtml). The e-waste dismantling town has an area of 52 km², and the distance between the north and south ends is about 9 km. The sampling range was set as a square of 9 km \times 9 km grid centered on an e-waste dismantling park to identify the VOC characteristics over the entire e-waste dismantling region. Considering the tremendous spatial heterogeneity of VOC concentration, the 9 km \times 9 km grid box was further divided into 81 smaller grid squares, and one sampling site was selected in every square based on the field survey. The ambient air surrounding the e-waste dismantling workshop was randomly sampled at nine sites in order to capture the ambient VOC characteristics adjacent to the e-waste dismantling activity. According to the population density and the land-use type, the sampling sites could be grouped into four categories, namely residential area 1 (R1), residential area 2 (R2), e-waste dismantling park (EP), and other areas (OA). According to the local residents and our field visits, R1 and R2 are both central residential areas. However, sporadic open burning of plastics was carried out by many plastic recycling workshops located in R1. Thus, R1 represents a mix of residential and industrial areas. Detailed information of the

sampling sites is shown in Fig. S1. Ambient air samples were sampled in cleaned and evacuated 2.7-L electro-polished stainless-steel canisters (ENTECH Instruments Inc., Silonite[™]). In order to better reflect the impact of environmental VOCs on the population, the sampling port was set at 1.5 m from the ground, significantly away from the auxiliary sampling vehicles. Each campaign was completed in one day to reduce the disturbance caused by weather and other factors.

2.2. VOC analysis

All air samples were qualitatively and quantitatively analyzed according to the USEPA method TO-15 and our previous studies (An et al., 2014b; He et al., 2015). Briefly, VOC samples were first concentrated using an Entech 7100 pre-concentrator (Entech Instruments Inc., CA, USA). Then, the highly concentrated VOCs were quickly desorbed and swept into the gas chromatography-mass spectrometry (GC-MS) system (7890B GC-5977C MS, Agilent Technologies, USA) for further separation and detection. A DB-5 column (60 m \times 0.32 mm \times 0.25 μ m, Agilent Technologies, USA) was employed to separate the VOC species. Detailed methods are described in Text S1 in the Supporting Information.

The VOC concentrations were quantified using the internal standard calibration method, estimated using 1 ppm standard samples Photochemical Assessment Monitoring Stations (PAMS) and 1 ppm TO-15 (Linde Spectra Environment Gases, USA). Four kinds of 1 ppm VOCs namely 1,4-difluorobenzene, chlorobenzened5, bromochloromethane, and 4-bromofluorobenzene (Linde Spectra Environment Gases, USA), were used as internal standards. The calibration curves were achieved by running diluted standards of gradient volume plus high purity nitrogen identically as the field samples. Standard samples were diluted using the Entech 4700 dynamic diluter. The target substances were identified from retention time and mass spectra using the NIST 05 database.

2.3. Quality control and assurance

Canisters were flushed with high purity nitrogen (99.99%) before being used and evacuated to less than 10 Pa after the cleansing procedures. After every 20 canisters, one was refilled with high purity nitrogen and then analyzed as a cleaning blank to ensure no target substance existed in the canister. All samples were examined twice within 20 days after sampling. All the calibration standard curves were justified with the correlation coefficients (R^2) over 0.99 (Table S2). The analytical system was checked daily with a one-point (typically 100 mL of 1 ppbv standard samples) calibration before running air samples. If the response was beyond $\pm 10\%$ of the initial calibration curve, a re-calibration was performed. The method detection limits (MDLs) were obtained by running 100 mL 1 ppbv standard sample seven times and multiplying the obtained standard deviation by 3.14. For all VOCs were maintained between 0.05 and 0.80 $\mu g~m^{-3}$ as presented in Table S2. Field blank and lab blank canisters were refilled with high purity nitrogen in the laboratory and analyzed after at least 24 h storage. All target compounds in the blank samples were below their MDLs.

2.4. Positive matrix factorization

Positive matrix factorization (PMF) model 5.0 was applied to determine the dominant VOC sources and quantify their contributions throughout the year. Briefly, the VOC data set can be considered a data matrix X of i (number of samples) by j (number of chemical species) dimensions. The PMF receptor model aims to determine the number of sources p that best characterize the VOC composition, with the species profile f of each source, and evaluate

the amount of mass *g* that contributed by each source to each individual sample, plus the residuals *e*. The mass balance equation is shown as follows:

$$X_{ij} = \sum_{k=1}^{P} g_{ik} f_{ki} + e_{ij}$$
(1)

Data were constrained by a penalty function so that no sample could have a negative source contribution and no species could have a negative concentration in any source profile. For a data set with m chemical species in n samples, the PMF solution with p independent sources minimized the object function Q, based on uncertainties (U):

$$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} \left[\frac{X_{ij} - \sum_{k=1}^{p} g_{ik} f_{ki}}{U_{ij}} \right]$$
(2)

The approaches for replacing and developing uncertainty values for missing and below-detection-limit data were obtained from the guide book. Briefly, values below the method detection limit (MDL) were substituted with MDL/2, and the missing values were substituted with median concentrations. If the VOC concentration was less than or equal to the MDL provided, the uncertainty was calculated using Eq. (3):

$$Unc = \frac{5}{6} \times MDL \tag{3}$$

If the VOC concentration is greater than MDL provided, the uncertainty was calculated as:

$$Unc = \sqrt{(Error \ Fraction \ \times \ Concentration)^2 + (0.5 \times MDL)^2}$$
 (4)

The Error Fraction can be set between 5% and 20%, depending on VOC concentrations (Buzcu and Fraser, 2006). In this study, the Error Fraction was set as 10%. Species categorizations were estimated based on the residuals and observed/predicted statistics after the initial base runs. Residual distributions should be within the range of -3 and +3, compounds having data percentage below detection limit exceeding 40% and low R² values (<0.5) would be not used in PMF analysis. Extra modeling uncertainty was set as 10% to account for spatial variation and changes in the source profiles. The concentration series of each pollutant were analyzed for extreme events that should be excluded from the analysis.

2.5. Health risk assessment for inhalation exposure

The health risks through inhalation of ambient VOCs were assessed using the hazard ratio (HR) and lifetime cancer risk (LCR) (Ramirez et al., 2012). The noncancer risk and cancer risk assessments were calculated following Eqs. (5)-(7):

$$EC_i = \frac{CA_i \times ET \times EF \times ED}{AT}$$
(5)

$$HR_i = \frac{EC_i}{RfC_i \times 1000} \tag{6}$$

$$LCR_i = EC_i \times UR_i \tag{7}$$

In these equations, EC_i represents the exposure concentration (µg m⁻³); CA_i represents ambient VOC concentration (µg m⁻³); ET represents exposure time per day (3.7 h per day as time spent outdoor); ED represents exposure duration (74.8 years); EF represents exposure frequency (365 days per year); AT represents

average lifetime (74.8 × 365 × 24 h); RfC_i is the reference concentration (mg m⁻³); UR_i represents the unit risk (µg m⁻³)⁻¹.

In this study, *ET*, *ED*, *AT* values were obtained from the literature (Li et al., 2020b). RfC_i (mg m⁻³) and UR values, mainly obtained from the USEPA (https://www.epa.gov/iris), are listed in Table S3, and missing values of some VOCs were obtained from existing research studies (Dumanoglu et al., 2014; Ramirez et al., 2012).

3. Results and discussion

3.1. The dominant ambient VOC species

The annual average concentrations of tested VOCs are listed in Table S2. The most abundant VOCs (mean \pm standard deviation) in the investigated areas were n-pentane (6.11 \pm 13.50 µg m⁻³), isopentane (13.36 \pm 38.65 µg m⁻³), benzene (3.75 \pm 7.03 µg m⁻³), toluene (11.81 \pm 24.24 µg m⁻³), ethylbenzene (2.31 \pm 5.22 µg m⁻³), p-xylenes (4.96 \pm 14.19 µg m⁻³), m-xylenes (2.22 \pm 6.09 µg m⁻³), o-xylenes (2.73 \pm 7.74 µg m⁻³), trichlorofluoromethane (CFC-11, 2.00 \pm 1.09 µg m⁻³), dichlorodifluoromethane (CFC-12, 3.96 \pm 2.06 µg m⁻³), 1,2-dichloropthane (1,2-DCA, 2.50 \pm 2.97 µg m⁻³), and 1,2-dichloropthane (1,2-DCP, 2.37 \pm 3.40 µg m⁻³).

The concentrations of the above species varied significantly in different seasons, especially between summer and winter. In summer, the average \pm standard deviation concentration of npentane, isopentane, benzene, toluene, ethylbenzene, p-xylene, mxylene, o-xylene, CFC-11, CFC-12, 1,2-DCA and 1,2-DCP were 4.00 ± 4.80 , 7.78 \pm 10.02, 1.97 \pm 3.74, 7.32 \pm 9.61, 1.22 \pm 1.61, $3.00 \pm 5.90, 1.10 \pm 1.90, 1.64 \pm 4.15, 3.24 \pm 1.24, 1.72 \pm 0.51,$ 1.21 \pm 3.33, and 1.43 \pm 1.83 μ g m⁻³, respectively. In addition, isopentane was the most abundant species in summer, followed by toluene. In contrast, their concentrations in the winter were higher than summer season with 1.8, 2.1, 3.3, 2.7, 2.9, 2.2, 2.8, 1.9, 1.4, 1.7, 3.8, and 2.5 times higher, respectively. Toluene was the most abundant VOC species in winter, followed by isopentane. Previous studies have reported that pentane and isopentane are the primary VOCs detected in gasoline exhausts and are ubiquitous pollutants in the ambient air (Song et al., 2020). For example, isopentane was the most abundant VOC species on the roadside in an urban area in Hanoi (Ly et al., 2020). BTEX is mostly emitted from industrial and vehicular sources. In the multi-industrial city of Ulsan, BTEX was reported as the most abundant VOC species (19.6 $\mu g m^{-3}$) (Kim et al., 2019), which was comparable to the corresponding median concentration of our research (12.52 $\mu g\,m^{-3}$). CFCs are typical longlived species in the atmosphere, mainly released from old refrigeration units, old air-conditioning, or foam products (Zhang et al., 2014). The mixing ratios of CFCs in the atmosphere were close to the background level in most cities of China (Fang et al., 2012), meaning that their concentrations were less affected by local emissions. 1,2-DCA is usually emitted from the vinyl chloride process in the petrochemical industry (Dumanoglu et al., 2014). 1,2-DCP is used as an industrial solvent and related to pesticides in rural areas (Ly et al., 2020; Ravina et al., 2020). It was reported that the levels of 1,2-DCA and 1,2-DCP were much lower in Beijing's atmosphere during the control period (Lin et al., 2016), during which typical industries, including petrochemical industries, were required to reduce or stop production in Beijing and surrounding provinces. As such, high levels of these VOC species found in this study could come from various sources other than e-waste dismantling. This increases the difficulty of analyzing the impact of e-waste dismantling on the surrounding ambient VOCs.

3.2. Seasonal variations

The ambient VOC concentration could vary with time due to interseasonal variations in meteorological conditions and emission intensities. We determined the seasonal pollution patterns of VOCs by comparing the VOC concentrations in four seasons and speculated the main influencing factors. We mainly focused on the total VOCs (TVOCs) and major VOC species since their seasonal variation was most apparent. In Fig. 1, the TVOC concentration refers to the sum of concentrations of 80 VOC species measured in our study. The measured VOCs were categorized into five groups: pentanes (n-pentane and isopentane), BTEX, CFCs (CFC-11, CFC-12, and CFC-113), 1,2-DCA, and 1,2-DCP depending on the emission source and relationship between each species.

The VOC concentrations varied significantly with seasons. For TVOCs, the variation trend was similar to different areas, with the highest concentrations in winter and autumn and lowest in summer and spring. High concentration of TVOCs in the wintertime was a result of meteorological factors. This is supported by the fact that the concentrations of CFCs were considerably higher in winter. Since there were no CFC emissions in winter, the higher concentration in winter could result from lower mixing height (Zhang et al., 2014). Thus, the poor diffusion conditions were speculated to be the reason for high wintertime VOC levels in these areas. This is a common occurrence, as high VOC concentrations were observed in the Bolu plateau in Turkey due to low mixing height (Dorter et al., 2020). Comparatively, high TVOC concentrations in autumn were only found outside the EP, indicating that they were influenced by emission events outside EP. During the autumn sampling period, the traffic density due to the autumn harvest. Gasoline exhausts and vehicular emissions could be the main contributors to high TVOC concentration outside EP in autumn, which was confirmed by high levels of pentanes and BTEX outside EP in autumn. This also explained why the concentration outside the dismantling park was closer to or higher than that inside the park in autumn, which didn't happen in other seasons.

The seasonal trend of BTEX was similar to TVOCs, which might be mainly influenced by diffusion conditions and traffic emissions. The seasonal variation of pentanes outside the EP was also similar to TVOCs and BTEX. In contrast, pentanes inside EP were the lowest in winter and the highest in summer, closely related to temperature. As many vehicles used by dismantling workers for commuting were parked in the park, pentanes might be volatilized from the fuels. The CFCs were higher in winter and summer outside EP, while only higher in winter inside EP. As production of CFCs has been completely phased out in China since 2008 (Wu et al., 2018), a higher CFC concentration might be related to the use of old air conditioning in the hot seasons (Zhang et al., 2014). In winter, the CFC levels inside EP were slightly higher than in other areas, which might be due to the leakage of waste cooling units (Kaya, 2016).

In the investigated areas, the levels of 1,2-DCA and 1,2-DCP were higher in autumn, and 1,2-DCA was high in winter. Besides, their levels were similar throughout the studied areas. As reported, 1,2-DCA is mainly used to synthesize vinyl chloride monomer and other chlorinated solvents (Dumanoglu et al., 2014). 1,2-DCA can also be used as a cleaning agent in household products and personal hygiene products (Ravina et al., 2020). 1,2-DCP is used as an industrial solvent in varnishes and paint stripper and could also be emitted by pesticide use (Ly et al., 2020; Ravina et al., 2020). Generally, both of them are classified as industrial solvents (Lin et al., 2016). As solvent factories are not widely distributed in the studied areas, high levels of these pollutants in autumn may come



Fig. 1. The seasonal variation of VOC concentration (μ g m⁻³) in typical areas. The box plot of each individual VOC represents the 25th and 75th percentile and the horizontal line inside the box indicates the median TVOCs. The circle symbol the average VOCs. Outliers are not shown in the figure.

from long-distance transport. Therefore, 72-h backward trajectories were modeled to provide possible transport pathways of the air masses arriving in this region. As shown in Fig. S2, air masses in summer and spring campaigns mainly arrived from the ocean, while air masses in winter and autumn campaigns come from continental areas, carrying pollutants from factories in other areas. During the winter campaign, city sewers were being laid, which greatly affected the local traffic in R1, leading to lower VOC levels.

As e-waste dismantling activities are relatively stable, the VOC emissions should not be affected widely by seasonal factors. Therefore, the concentrations of VOCs in EP should be in the same range in other seasons, except for winter, during which the VOC concentration increased due to the accumulation in the air (Dorter et al., 2020). As shown in Fig. 1, out of all the compounds discussed, the TVOCs, BTEX, and CFCs conformed to this rule. Since CFCs in the background air also followed this rule, we preliminarily believe that BTEX were related to the dismantling of e-waste, and TVOCs in EP were strongly influenced by e-waste dismantling.

The VOC concentration varied significantly during different seasons. The seasonal trends were due to the combined effect of meteorological and emission source factors. Higher VOC levels were generally observed in winter and autumn. Besides, it can be seen that the VOC levels in EP were always high during all seasons, indicating a strong emission source of these hazardous compounds.

3.3. Spatial distribution

The spatial distribution of VOCs is closely related to the

pollution sources. Spatial maps of VOCs were created to explore their spatial distribution and the impact of e-waste dismantling on the surrounding environment. We mainly focused on the compounds with implications for human health, namely BTEX, 1,2-DCP, and 1,2-DCA. As Fig. 2 shows, there were apparent changes in the VOC spatial distribution of different seasons. The BTEX hotspots included EP, R1, and R2. In the winter and autumn, higher BTEX concentrations were observed at rural sites. The possible reason could be the increased traffic activities in rural areas due to the autumn harvest in the autumn; while in winter, it may be the diffusion from EP, R1, and R2, as the rural ambient VOCs could be influenced by nearby sources (Kumar et al., 2018). Stable atmospheric conditions in wintertime led to the accumulation of pollutants and the subsequent increase in concentration. In spring and summer, BTEX mainly concentrated in EP and R1, as the e-waste dismantling activities emitted BTEX in all seasons, and the plastic solid-waste recycling activity might also contribute partly to BTEX (He et al., 2015; Lu et al., 2014). It can be seen that EP was a hotspot of BTEX, but the impact of the source was relatively small.

The concentrations of 1,2-DCA and 1,2-DCP were low in R1 and R2 except in autumn and winter, suggesting that these pollutants did not come from urban sources. In contrast, they were mainly distributed in the EP and OA. Therefore, these sources might be emitted by natural sources, agricultural, or industrial activities (Li et al., 2008). The spatial distribution of these compounds is almost identical in autumn, indicating that they might come from similar sources. Furthermore, as their distribution was uniform across the investigated area with no apparent emission source, we



Fig. 2. The spatial distributions of VOC mass concentration (µg m⁻³) different seasons. The order from left to right was winter, spring, summer and fall.

speculated that they were from long-range transport. In winter, the concentrations of 1,2-DCA in the study region were relatively high, like autumn. However, the concentration and distribution of 1,2-DCP were not consistent with 1,2-DCA. Therefore, these VOCs might come from different sources in winter. 1,2-DCA and 1,2-DCP may vary in space and have no stable distribution pattern in different seasons. However, EP was a hotspot of 1,2-DCA in winter and autumn, while a hotspot of 1,2-DCP in spring and summer. In summer, the distribution patterns of these two pollutants were similar. We also found that two hotspots were the EP and an Underwear factory. This indicated that the e-waste dismantling activities could contribute to the emission of these pollutants, though not continuously. In addition, we can also observe from Fig. 2 that the hotspot area centered on EP was larger for BTEX than 1,2-DCA and 1,2-DCP, partly because the photodegradation rate of BTEX is faster in the diffusion process.

In conclusion, the VOC distribution varied significantly during different seasons. The distributions of BTEX, 1,2-DCA, and 1,2-DCP were all related to the e-waste dismantling activities. EP was a hotspot of these three species; however, other hotspots of these health-related pollutants also existed.

3.4. Source apportionment

As the VOCs from the e-waste dismantling process can significantly influence the ambient air, the source apportionments were conducted in each area using PMF 5.0 to quantify the contribution from the e-waste dismantling activities. Factor number was obtained from the results of the principal component analysis using SPSS 25. The factor extraction method was based on the eigenvalue set greater than 0.5 (An et al., 2014a; Bozkurt et al., 2018). The R1, R2, OA, and EP factor numbers were 4, 4, 6, and 5, respectively. The r² of the observed and predicted total concentrations were all above 0.9 in each area. Details of the PMF diagnosis results are listed in Table S4 in the supplementary materials. PMF analysis revealed



Fig. 3. Source profiles for the five-factor solution in EP derived from PMF model.

that the e-waste emission source contributed only to the ambient VOC pollution in EP and not in other areas. The identified source profiles of EP are illustrated in Fig. 3, while the source profiles of other areas are illustrated in Fig. S3.

It has been reported that pentane, isopentane, and BTEX are abundant VOC species of gasoline exhaust (Watson et al., 2001). Therefore, factor 1 in Fig. 3 is termed as the gasoline exhaust. Factor 2 is rich in n-pentane and isopentane but less in benzene series. This source may come from fuel volatilization or incomplete combustion. Accordingly, factor 2 is defined as gasoline evaporation. Factor 3 is represented by CFCs and carbon tetrachloride, long-lived atmospheric substances (Sarkar et al., 2018). Therefore, factor 3 is termed as background. Factor 4 is represented by 1,2-DCP. In addition to long-distance transport, e-waste dismantling also produces 1,2-DCP (Liu et al., 2017); thus, factor 4 represents long-distance transport and e-waste emission. Factor 5 contains a large number of BTEX, CFCs, and 1,2-DCA. It has been reported that e-waste dismantling leads to large-scale emissions of BTEX and 1,2-DCA (Liu et al., 2017). As a result, factor 5 is termed e-waste. Interestingly, many CFCs existed in this source, indicating that e-waste dismantling may contribute to CFCs in the ambient air, which might be another environmental hazard caused by e-waste dismantling.

As for other investigated areas, the factor profiles of R1 and R2 were similar. Besides gasoline exhausts and background, longrange transport dominated by 1,2-DCA and 1,2-DCP and solvent use dominated by BTEX (Watson et al., 2001) were the other two sources. In R1 and R2, the 1,2-DCA and 1,2-DCP mainly came from the long-range transport in autumn. The similarity between R1 and R2 indicated that the local plastic recycling activity had no influence on the VOC pollution in these residential areas. In OA, 1,2-DCA and 1,2-DCP were divided into two different pollution sources. 1,2-DCA could be discharged randomly by the residents' living pollution since there are no municipal facilities in remote areas. As such, 1,2-DCA in some rural sites was higher than R1 and R2. In addition, many crops were grown in OA, and 1,2-DCP might be released when the pesticide was sprayed. Therefore, 1,2-DCA and 1,2-DCP were from different sources in OA, namely transport & pesticide and transport & domestic.

Furthermore, the source contributions in each area are shown in Fig. 4. Gasoline exhaust was the most dominant source in R1, R2, and OA. In contrast, gasoline evaporation in EP (29%) and e-waste dismantling contributed 20% to the total VOCs. No e-waste

pollution source was observed in residential and remote areas. This may be because the sampling points were too scattered, or the number of samples analyzed was relatively small. Therefore, further investigation is needed. According to the distribution of pollutants, e-waste dismantling activity was likely to impact the adjacent areas. Future research should focus on residential areas adjacent to the e-waste dismantling park and analyze the pollution sources employing continuous sampling at fixed points.

3.5. Health risk assessment

In order to assess the health risks from the exposure to VOCs released in the studied areas, a comprehensive exposure risk assessment was conducted. To comprehensively evaluate the health risks, all the health-related compounds in this study were assessed. As a result, a total of 9 carcinogenic and 24 non-carcinogenic VOCs were calculated.

As per previous studies (Li et al., 2013; Ramirez et al., 2012; Zheng et al., 2020), compounds with a cancer risk of over 1.0×10^{-4} were considered as a "definite risk", between 1.0×10^{-5} and 1.0×10^{-4} as a "probable risk", between 1.0×10^{-5} and 1.0×10^{-6} as a "possible risk", lower than 1.0×10^{-6} as "negligible". As shown in Fig. 5, the cancer risks of 1,2-DCA, 1,2-DCP, and 1,3-butadiene were larger than 1.0×10^{-6} outside the EP, while benzene was also slightly higher than 1.0×10^{-6} in R2. As per the results of source analysis, these compounds mainly came from long-range transport and vehicular emission. In contrast, two more species (ethylbenzene and chloroform), which posed a definite cancer-risk in the EP, mainly came from the e-waste dismantling process, indicating higher cancer risk caused by e-waste dismantling activities in EP.

Noncancer risks from exposure to 25 VOC species in all studied areas were also evaluated. As shown Table S5, the noncancer risks were in order of EP (0.36) > R2 (0.29) > R1 (0.17) > OA (0.16).



Fig. 4. VOCs source contributions of each area resolved using PMF model.



Fig. 5. Cancer risks from inhalation exposure to VOCs in different areas.

According to the previous works (Hoddinott and Lee, 2000), the results indicate that the noncancer risks in all areas were below the threshold and could be ignored.

Overall, the health risk was most severe in the EP, indicating the considerable health impact of e-waste dismantling activities. It worth noting that cancer risk evaluation was based on the average VOC concentration of each area, which may lead to an underestimation of the risk in some areas. For long-term outdoor workers, the health risk might be even higher.

4. Conclusions

Based on multi-site sampling, VOCs in a typical e-waste dismantling region in southeastern China were monitored during four seasons by grid-sampling. The dominant VOC species included n-pentane, isopentane, BTEX, CFCs, 1,2-DCA, and 1,2-DCP. Seasonal VOC trend analysis indicated seasonal pollution characteristics in different areas. VOC concentration was affected by meteorological conditions and emission sources, and long-range transport. VOC pollution was most severe in winter and autumn. The spatial distribution analysis revealed that the e-waste dismantling park was a hotspot of BTEX, 1,2-DCA, and 1,2-DCP, while these compounds also came from other sources. PMF source apportionment found no contribution of the e-waste dismantling activity to the VOCs outside the e-waste dismantling park. In contrast, 20% of total VOCs in the e-waste dismantling park came from the e-waste dismantling process.

Finally, health risk evaluations showed that the population in the studied areas were under probable cancer risk from exposure to three or four compounds and under probable cancer risk from exposure to two more species in the e-waste dismantling park. Nevertheless, the noncancer risk was negligible. Both cancer and noncancer risks were mainly caused by 1,3-butadiene, 1,2-DCA, and 1,2-DCP.

This study complements knowledge of chemical pollution associated with e-waste dismantling. We found that a centralized dismantling area of e-waste is a VOC pollution hotspot. People in areas adjacent to this activity can suffer from serious health risks due to the exposure to VOCs emitted. More attention should be paid to the VOC pollution caused by e-waste dismantling.

Author statement

Daijin Chen: Methodology, Formal analysis, Writing-original draft. Ranran Liu: Methodology, Formal analysis. Qinhao Lin: Methodology, Formal analysis. Shengtao Ma: Methodology, Data curation. Guiying Li: Writing- Reviewing and Editing. Yingxin Yu: Visualization, Investigation. Chaosheng Zhang: Validation. Taicheng An: Conceptualization, Supervision.

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.chemosphere.2021.130022.

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