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# Characterization and risk assessment of total suspended particles (TSP) and fine particles ( $PM_{2.5}$ ) in a rural transformational e-waste recycling region of Southern China



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#### HIGHLIGHTS

- TSP and PM<sub>2.5</sub> composition around ewaste recycling region were determined.
- Levels of TSP and PM<sub>2.5</sub> were lower with advanced recycling methods.
- High positive correlations between Cu and both W and Te levels were found.
- · High carcinogenic risks were found.

# GRAPHICAL ABSTRACT



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# ABSTRACT

In 2016, total suspended particles (TSP) and fine particles ( $PM_{2.5}$ ) were collected near four e-waste recycling parks in a region of Southern China. TSP and  $PM_{2.5}$  levels and composition around these industrial activities were determined and the potential risks for human health due to the exposure to toxic elements contained on fine particles ( $PM_{2.5}$ ) were evaluated. Levels of TSP and  $PM_{2.5}$  were lower with advanced recycling methods than with small recycling e-waste workshops operating in the sampling region. The main trace elements in particles were Cu, Pb, and Ti, the same as those detected before the transition to advanced dismantling methods in e-waste recycling. Significantly higher levels of Cu, Pb, Sn, Te, Tl and  $NH_4^+$  in TSP and Cu and Te in  $PM_{2.5}$  were found in e-waste recycling areas than in BG site. Taking Cu as the indicative element emitted from e-waste recycling activities, significant high positive correlations between Cu and W, and Cu and Te were found. These elements are present and can be released from electrical and electronical components during e-waste recycling processes. Exposure to elements for the population living near these e-waste recycling parks means carcinogenic risks above the acceptable threshold (>10<sup>-5</sup>). © 2019 Elsevier B.V. All rights reserved.

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Science or re Total Environment



# 1. Introduction

Air pollution has become a global environmental problem in low, middle and high-income countries. Around 4.2 million per year of premature deaths are associated with air pollution (WHO, 2018). Particulate matter (PM), as a primary contributor for air pollution (Cohen et al., 2005), plays a significant role not only in reducing the visibility of air, but also in leading to adverse health effects (Zhang et al., 2012). There are many studies confirming that PM can induce a series of health problems including -but not limited to- cardiovascular and pulmonary diseases (Anderson et al., 2012; Brook et al., 2010; Pope and Dockery, 2012; Yu et al., 2019). These adverse health effects depend on the sizes and composition of PM, which are influenced by the meteorological conditions and the characteristics of the emission sources (Cassee et al., 2013; Deng et al., 2019). Total suspended particles (TSP) and PM<sub>2.5</sub> are two representative types of airborne PM with different aerodynamic diameters. In turn, the compositions of both can be divided into six parts: mineral matter, organic matter and elemental carbon (OM + EC), secondary inorganic aerosols (SIA), sea spray, trace elements and unaccounted, the difference between the PM concentration and the sum of the rest of fractions (Rovira et al., 2018; Sánchez-Soberón et al., 2019).

*E*-waste is defined as discarded electronic products constituted by heterogeneous and complex materials. Many substances that are contained in these materials, such as heavy metals, flame retardants and plasticizers, among others, may be highly toxic (Robinson, 2009). China used to import 90% of the waste transferred to Asia (UNEP, 2005), where e-waste was usually dismantled to recover precious metals in small family workshops, with rough disassembly technologies (for instance, open burning and acid washing). The deteriorated environment triggered Chinese government to ban the scattered e-waste recycling activities, which are replaced by dismantling industrial parks. Organic pollutants such as, polycyclic aromatic hydrocarbons, flame retardants and plasticizers, have been frequently detected in airborne particles from both, formal and informal e-waste recycling activities. (Chen et al., 2016, 2019; Ren et al., 2015; Song and Li, 2014; Xiao et al., 2014). The levels of several heavy metals in PM from different ewaste recycling regions have been reported in recent years (Awasthi et al., 2016; Bi et al., 2010; Gangwar et al., 2019). However, information on other chemical components of PM in e-waste recycling areas is still limited. On the other hand, little is known about the influence of transition from informal to formal e-waste recycling on the emission of atmospheric particles. Moreover, these pollutants can have adverse effects on the health of the population living near e-waste recycling parks.

In this study, we determined the concentrations of mineral and trace elements, as well as water-soluble ions in TSP and  $PM_{2.5}$  collected around four e-waste recycling parks and a background area in the south of China after scattered e-waste recycling activities were banned by local government. The aims of the study are the following: i) to determine levels and chemical compositions of these particles after the transition of e-waste recycling activities; ii) to examine the characteristic components of particles associated with the formal e-waste recycling activities in the region of sampling; and iii) to evaluate the potential risks for human health due to exposure to toxic elements contained on fine particles ( $PM_{2.5}$ ).

#### 2. Materials and methods

#### 2.1. Sites description and sampling

TSP and PM<sub>2.5</sub> were collected around four e-waste recycling parks (E1, E2, E3 and E4) in a rural region of Qingyuan, southern China, in October–November of 2016 (Fig. 1). This region is one of the biggest recycling e-waste sites in China, where e-waste recycling activities have been conducted for >30 years (Xiao et al., 2014). However, with the introduction of new local policy, scatter e-waste dismantling

workshops were replaced by formal dismantling parks from 2015 (Liu, 2015). Samplers were placed on the roof (10 m above the ground), near (between 270 and 800 m), and downwind of the e-waste recycling parks. The background site (BG) was located at an adjacent rural region which at the southeast and 20 km far away from the sampling region. There is no significant industrial activity around background site. Samples in background sites were collected, when the winds direction was blowing from southeast.

In each sampling site, 24-h samples of TSP and PM<sub>2.5</sub> were collected on quartz fibber filters (QFFs) during five consecutive days (n = 5), except in BG site where only two samples were collected. The QFFs were pre-treated at 450 °C for 4 h, and conditioned at 25 °C and 40% relative humidity for 24 h. Two high-volume active samplers were used to collect samples simultaneously in each site, one for PM<sub>2.5</sub> at a flow of 1.13 m<sup>3</sup>/min (TE-6001, Tish Environment Inc., Ohio, USA) and another for TSP, at a flow of 0.28 m<sup>3</sup>/min (ASM-1, Mingye Environmental Protection Technology Co., Ltd., Guangzhou, China). The campaigns were conducted from E1 to E4 with the same two samplers. After sampling, QFFs were wrapped in aluminum foils and conditioned at 25 °C and 40% relative humidity for 24 h to obtain the weight. Finally, these QFFs were stored at -20 °C until analysis.

#### 2.2. Organic carbon (OC), elemental carbon (EC), and organic matter (OM)

A piece of each filter (0.525 cm<sup>2</sup>) was cut for analysing organic (OC) and elemental carbon (EC) with a carbon analyser (DRI Model 2001 Organic Carbon/Elemental Carbon Analyser, Atmoslytic Inc.) (Ding et al., 2018). For OM calculation OC was multiplied by a factor of 1.6 (Rovira et al., 2018).

#### 2.3. Chemical elements

An eighth part of each filter was used to analyze chemical elements. Filters were digested with 2 mL of 65% nitric acid (Suprapur, E. Merck, Darmstadt, Germany) and 3 mL of hydrofluoric acid (Suprapur, E. Merck, Darmstadt, Germany) in Teflon vessels. After 8 h at room temperature, and 8 h at 80 °C, digested samples were evaporated in a sand bath. Digested samples were resuspended with 2.5 mL 65% nitric acid. Solutions were then transferred to a 25 mL volumetric flask, and ultrapure water was added. Extracts were kept frozen at -20 °C until analysis. Most trace elements (Al, As, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, La, Li, Hg, Mn, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sr, Tb, Th, Ti, Tl, U, V, W, Y, Yb, and Zr) were analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer Elan 6000), while Ba, Ca, Fe, K, Mg and Na were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer Optima 3200RL).

## 2.4. Ions

A portion of the filter was disposed to analyze ions. Filters were extracted with 15 mL of ultrapure water through axial agitation for 12 h and sonicated at 60 °C for 10 min. The mixtures were filtered with a 0.47 µm membrane filter. The concentrations of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup> were determined by ion chromatograph (Dionex D-300), while those of NH<sub>4</sub><sup>+</sup> were determined by the reaction of Berthelot. Furthermore, the levels of CO<sub>3</sub><sup>2-</sup> and SiO<sub>2</sub> were calculated from stoichiometric ratios, which are CO<sub>3</sub><sup>2-</sup> = 1.5Ca + 2.5 Mg and 2Al<sub>2</sub>O<sub>3</sub> = SiO<sub>2</sub>. In turn, all of the aluminum was assumed to be present in oxide form.

## 2.5. Particle characterization

Particle matter (PM) was divided into six main components: mineral matter (sum of  $CO_3^{2-}$ , SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Ti, P, Mn, Mg, K, Fe and Ca), sea spray (sum of Na<sup>+</sup> and Cl<sup>-</sup>), OM + EC, secondary inorganic aerosols (sum of SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>), trace elements (sum of the rest of elements), and



Fig. 1. Sampling sites near e-waste recycling parks (E1, E2, E3 and E4) and a background (BG) location.

unaccounted (the difference between the PM concentration and the sum of the rest of fractions).

# 2.6. Quality assurance and quality control (QA/QC)

Field blanks, procedural blanks, duplicate samples and standards (Standard Reference Material 1648a Urban Particulate, National Institute of Standards and Technology and Standard sucrose solution, Merck, Darmstadt, Germany) were used for quality assurance and quality control. The detection limits (DLs) of OC and EC were 0.11 µg C/m<sup>3</sup> and 0.05 µg C/m<sup>3</sup>, respectively. The DLs of trace elements were 0.06 ng/m<sup>3</sup> for Ce, Cs, Dy, Er, Eu, Gd, Ho, La, Nd, Pr, Sm, Tb, Th, Tl, U, Y and Yb; 0.12 ng/m<sup>3</sup> for Ba, Bi, Cd, Co, Li, Nb, Pb, Rb, Sb, Sr, Ta, Te and

W; 0.24 ng/m<sup>3</sup> for Hg and Mn; 0.59 ng/m<sup>3</sup> for Be, Cu, and Sn; 1.18 ng/m<sup>3</sup> for As, Ge, Hf, Ni, Ti, and Zr; 2.35 ng/m<sup>3</sup> for Cr, Mo and Zn, 3.53 ng/m<sup>3</sup> for Sc and V; 5.88 ng/m<sup>3</sup> for Se; 11.8 ng/m<sup>3</sup> for Fe; 58.8 ng/m<sup>3</sup> for Al, B, Ca and Mg; 588 ng/m<sup>3</sup> for K, P; 1176 ng/m<sup>3</sup> for Na. Finally, the DLs of ions were: 0.04 µg/m<sup>3</sup> for Cl<sup>-</sup>, 0.08 µg/m<sup>3</sup> for NO<sub>3</sub><sup>-</sup>, 0.20 µg/m<sup>3</sup> for SO<sub>4</sub><sup>2-</sup> and 0.008 µg/m<sup>3</sup> for NH<sub>4</sub><sup>+</sup>. The concentrations of samples whose values were below the respective DL were considered as one-half of that limit (ND = 1/2 DL).

# 2.7. Human exposure and health risks assessment

The calculations for human exposure and health risks assessment have been described in recent studies (Rovira et al., 2010; SánchezSoberón et al., 2015). Briefly, exposure was estimated by considering only the inhalation route for an average adult in a mean daily routine. Eq. (1) was used for evaluating exposure, being expressed as:

$$Exp = \frac{C_{air} \times IR \times EF \times AcT}{BW \times 365 \times 24}$$
(1)

where  $C_{air}$  is the indoor or outdoor air concentration of each element.  $C_{air}$  for outdoor concentrations were obtained from outdoor sampling, while indoor concentrations were calculated from outdoor concentrations through the software IAQX v 1.1 (PM), developed by the USEPA. In the current study, we set an average room volume of 30 m<sup>3</sup>, with ventilation rate at 0.50 1/h. Deposition rates and infiltration factor size were calculated from He et al. (2005), and Chen and Zhao (2011), which were 0.52 and 0.61 1/h, respectively. Inhalation rate (IR) in sleeping, work/leisure and outdoor were 7.58, 38.8 and 38.8 m<sup>3</sup>/day, respectively (OEHHA, 2012). Exposure frequency (EF) was considered as 350 days/year. Activity times (AcT) for sleeping, work/leisure and outdoor were 8.88, 12.7, 2.40 h/day (Idescat, 2012). Body weight (BW) was set at 70 kg.

Three Eqs. (2)-(4) were used for assessing human health risks:

Exposure concentrations(EC) = 
$$\frac{C_{air} \times AcT \times EF \times ED}{AT \times 365 \times 24}$$
 (2)

Hazard Quotient (HQ) = 
$$\frac{\text{EC} \times 10^6}{\text{RfC}}$$
 (3)

$$CancerRisk = EC \times 10^6 \times IUR$$
(4)

where ED is exposure duration, which was set at 30 years (US EPA, 1989); AT is averaging time: 70 years for carcinogenic risk calculations, and 30 years for non-carcinogenic risk calculations (US EPA, 1989); RfC and IUR, which are displayed in Table S1, are the reference inhalation concentration and inhalation unit risk, respectively. Exposure and risk assessment were conducted only with breathable particles (PM<sub>2.5</sub> in present study) and for those elements that have defined their respective toxicological files (As, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, Se, V and U).

#### 2.8. Data analysis

For the statistical analysis, values below the detection limit (LD) were assumed to be equal to one-half of that limit (ND =  $\frac{1}{2}$  LD). Statistical analysis of data was performed by GraphPad Prism V5.0.3.477 and IBM SPSS Statistics (v 25.0). Firstly, Levene test was applied to establish the parametric distribution of data. Subsequently, the ANOVA or Kruskal-Wallis tests were applied. A difference was considered as statistically significant when the probability was lower than 0.05 (*p* < 0.05). Two-tailed Pearson test was used to determine the correlation at a confidence interval of 95%.

## 3. Results and discussion

#### 3.1. Characterization of TSP and PM<sub>2.5</sub>

### 3.1.1. Levels of TSP and PM<sub>2.5</sub>

Levels of TSP and PM<sub>2.5</sub> in the four e-waste recycling parks and background area are depicted in Fig. 2. Concetrations of TSP ranged from 90.8  $\pm$  15.5 µg/m<sup>3</sup> at E3 to 137  $\pm$  53.2 µg/m<sup>3</sup> at E4, while PM<sub>2.5</sub> levels ranged from 42.8  $\pm$  4.93 µg/m<sup>3</sup> at E1 to 75.5  $\pm$  29.4 µg/m<sup>3</sup> at E2. Regarding TSP, significant (p < 0.05) differences were noted between background area (BG) (168 µg/m<sup>3</sup>) and two e-waste recycling parks (E1 (94.5 µg/m<sup>3</sup>) and E3 (90.8 µg/m<sup>3</sup>)), however not significant (p > 0.05) differences were detected in PM<sub>2.5</sub> levels between background area than e-waste recycling parks (considered individually or all together). According to Chinese legislation (GB 3095–2012) daily limits for PM<sub>2.5</sub> and TSP are set at 75 µg/m<sup>3</sup> and 300 µg/m<sup>3</sup>, respectively. This means that the daily



**Fig. 2.** Total suspended particles (TSP) and  $PM_{2.5}$  levels (average + standard deviation) in the four sampling sites around e-waste recycling parks (E1, E2, E3 and E4) and in a background (BG) location.

concentrations of PM<sub>2.5</sub> frequently exceeded the limits in E2 and E4. In addition, PM<sub>2.5</sub> levels were much higher than the threshold values of the World Health organization (WHO) (10 and 25  $\mu$ g/m<sup>3</sup> for annual and daily means, respectively) and those of the European Union (25  $\mu$ g/m<sup>3</sup> for annual mean). The average PM<sub>2.5</sub> concentration between 2013 and 2014, measured by Ding et al. (2018) in the same region, when informal e-waste workshops were operating, was 182  $\pm$  62.0  $\mu$ g/m<sup>3</sup>, twice higher than that found in the present study. Comparing with data from other e-waste recycling regions, the concentrations of PM<sub>2.5</sub> in Guiyu in 2017 (mean level = 39.1  $\mu$ g/m<sup>3</sup>) were lower than those found in the current survey (Zhang et al., 2019), while the levels of PM<sub>10</sub> between 193 and 243  $\mu$ g/m<sup>3</sup> were recently reported from illegal e-waste burning regions in India (Gangwar et al., 2019).

## 3.1.2. Mineral and trace elements

Table 1 shows the concentrations of trace elements in both  $PM_{2.5}$  and TSP. In  $PM_{2.5}$  samples, Be, Hf, Hg, Ho, Nb, P, Sc, Se, Ta, Tb and Th levels were not detected in any of the 4 sampling sites, while levels of Ba, Cr, Eu, Sr were detected only in E1. The rest of analyzed elements could be detected in all samples collected in the surroundings of the e-waste recycling parks, with the exceptions of V in E3, and Te in E1. The main elements in  $PM_{2.5}$  were Na, followed by Ca, K, Al, Fe and Mg. The most abundant trace elements in E2, E3 and E4 were Cu, Pb, Mo, Ti, while E1 was dominated by Ba, Cu, Pb and Ni.

#### Table 1

Levels (mean ± SD) of trace elements in PM<sub>2.5</sub> and TSP samples collected in 2016 near four e-waste recycling parks (E1, E2, E3 and E4) and a background area (BG).

	PM <sub>2.5</sub>					TSP				
	E1	E2	E3	E4	BG	E1	E2	E3	E4	BG
	(n = 5)	(n = 5)	( <i>n</i> = 5)	(n = 5)	( <i>n</i> = 2)	(n = 5)	(n = 5)	(n = 5)	(n = 5)	(n = 2)
Al	$915\pm340$	$621\pm 645$	$785\pm439$	$841\pm651$	$568 \pm 337$	$1267\pm937$	$1267\pm937$	$665\pm402$	$2641 \pm 1194$	$3620\pm2669$
As	$13.0 \pm 5.33$	$12.1\pm6.84$	$9.26 \pm 4.64$	$7.35 \pm 3.67$	$6.64 \pm 1.19$	$22.6 \pm 9.97$	$16.6\pm10.2$	$11.7 \pm 3.72$	$12.3\pm6.90$	$22.6\pm20.3$
Ba	$264\pm65.9$	ND	ND	ND	$235\pm38.5$	ND	ND	ND	ND	$977\pm379$
Bi	$3.72\pm1.15$	$2.79 \pm 1.23$	$3.31 \pm 1.07$	$3.37\pm2.76$	$1.34\pm0.06$	$3.90\pm1.38$	$3.23\pm1.42$	$4.28 \pm 1.31$	$3.82\pm2.74$	$3.76 \pm 1.85$
Ca	$4229\pm319$	$4035\pm479$	$3956 \pm 485$	$4282\pm937$	$4011\pm396$	$5242\pm844$	$5708 \pm 1354$	$5420 \pm 936$	$8641 \pm 1829$	$21,100 \pm 11,943$
Cd	$3.92\pm1.63$	$3.23 \pm 2.24$	$3.80\pm3.63$	$3.15\pm2.16$	$2.66 \pm 1.80$	$4.59 \pm 1.64$	$3.32\pm2.57$	$6.85 \pm 9.04$	$3.69 \pm 1.79$	$4.54\pm0.42$
Ce	$1.09\pm0.24$	$1.27\pm0.23$	$0.98\pm0.22$	$1.26\pm0.56$	$1.14\pm0.28$	$1.04\pm0.72$	$2.23\pm1.27$	$0.93\pm0.50$	$2.49 \pm 2.43$	$9.03 \pm 6.87$
Со	$0.42\pm0.17$	$0.29\pm0.14$	$0.26\pm0.09$	$0.27\pm0.17$	$0.42\pm0.09$	$0.95\pm0.59$	$0.62\pm0.44$	$0.67\pm0.35$	$1.06\pm0.63$	$2.87 \pm 2.54$
Cr	$34.7 \pm 4.21$	ND	ND	ND	$39.1 \pm 9.61$	$53.8 \pm 11.2$	ND	ND	ND	$180 \pm 81.4$
Cs	$0.46\pm0.13$	$0.25\pm0.14$	$0.26\pm0.14$	$0.37 \pm 0.19$	$0.54\pm0.003$	$0.39 \pm 0.15$	$0.52 \pm 0.33$	$0.33 \pm 0.15$	$0.57 \pm 0.31$	$0.60\pm0.20$
Cu	$221 \pm 127$	$242\pm143$	$83.5 \pm 17.1$	$102 \pm 93.0$	$32.4 \pm 1.77$	$373 \pm 202$	$894 \pm 581$	$134 \pm 16.0$	$368 \pm 305$	$284 \pm 229$
Dy	$0.19\pm0.03$	$0.17 \pm 0.05$	$0.22\pm0.06$	$0.22 \pm 0.09$	$0.14\pm0.02$	ND	ND	ND	ND	$0.25\pm0.04$
Er	$0.09\pm0.02$	$0.06\pm0.04$	$0.09\pm0.03$	$0.09 \pm 0.05$	ND	ND	ND	ND	ND	$0.09\pm0.02$
Eu	$0.07\pm0.01$	ND	ND	ND	$0.10\pm0.02$	ND	ND	ND	ND	$0.39 \pm 0.15$
Fe	$377 \pm 71.5$	$422 \pm 134$	$337 \pm 102$	$342 \pm 103$	$471 \pm 202$	$1126 \pm 332$	$1369 \pm 453$	$1111 \pm 320$	$1564 \pm 546$	$4025 \pm 3518$
Gd	$0.17 \pm 0.02$	$0.16 \pm 0.02$	$0.17 \pm 0.04$	$0.18 \pm 0.06$	$0.12 \pm 0.01$	ND	ND	ND	ND	$0.48\pm0.07$
Ge	$1.31 \pm 0.46$	$1.12 \pm 0.50$	$1.22 \pm 0.37$	$1.30 \pm 0.71$	$1.38 \pm 0.12$	ND	ND	ND	ND	$5.80 \pm 3.23$
Hg	ND	ND	ND	ND	ND	ND	$0.20 \pm 0.12$	ND	ND	ND
K	$1375 \pm 268$	$1101 \pm 372$	$643 \pm 333$	$939 \pm 501$	$1187 \pm 107$	$1506 \pm 408$	$1017 \pm 521$	ND	$772 \pm 556$	$6137 \pm 3701$
La	$0.52 \pm 0.10$	$0.56 \pm 0.13$	$0.47 \pm 0.15$	$0.49 \pm 0.14$	$0.53 \pm 0.12$	$0.22 \pm 0.20$	$0.63 \pm 0.44$	$0.35 \pm 0.23$	$0.79 \pm 0.78$	$3.22 \pm 2.23$
Li	$1.47 \pm 0.51$	$1.31 \pm 0.42$	$1.12 \pm 0.34$	$1.51 \pm 0.64$	$1.20 \pm 0.43$	$0.45 \pm 0.53$	$0.97 \pm 0.94$	$0.46 \pm 0.37$	$1.30 \pm 1.48$	$4.01 \pm 3.41$
Mg	$252 \pm 332$	$497 \pm 425$	$745 \pm 332$	$877 \pm 631$	ND	ND	ND	ND	ND	ND
Mn	$20.4 \pm 5.99$	$25.6 \pm 7.97$	$18.3 \pm 5.14$	$23.2 \pm 10.5$	$29.6 \pm 9.03$	$40.9 \pm 14.1$	$53.0 \pm 16.3$	$40.3 \pm 11.3$	$61.9 \pm 22.4$	$133 \pm 107$
No	$38.9 \pm 7.78$	$56.0 \pm 6.19$	$54.4 \pm 7.36$	$5/.1 \pm 15.4$	$41.5 \pm 7.89$	ND	ND	ND	ND	$181 \pm /9.3$
Na	$10,500 \pm 960$	$11,244 \pm 405$	$10,460 \pm 1008$	$11,/14 \pm 2503$	$9592 \pm 2587$	$11,261 \pm 10/0$	$14,6/6 \pm 1430$	$12,/16 \pm 1522$	$14,389 \pm 4291$	$43,896 \pm 19,279$
INC	$0.44 \pm 0.06$	$0.49 \pm 0.10$	$0.49 \pm 0.10$	$0.40 \pm 0.08$	$0.42 \pm 0.03$	$0.12 \pm 0.11$	$0.56 \pm 0.41$	$0.39 \pm 0.30$	$0.62 \pm 0.59$	$2.58 \pm 1.53$
INI Dl	$91.7 \pm 11.0$	$10.2 \pm 2.12$	$10.0 \pm 1.61$	$12.2 \pm 2.20$	$78.8 \pm 21.3$	$193 \pm 12.0$	$12.5 \pm 4.42$	$11.5 \pm 2.38$	$16.6 \pm 3.50$	$380 \pm 144$
PD Dr	$121 \pm 64.9$	$91.6 \pm 60.6$	$85.0 \pm 23.0$	$78.2 \pm 40.2$	$30.1 \pm 5.03$	$145 \pm 75.6$	$113 \pm 79.2$	$126 \pm 34.0$	$183 \pm 131$	$89.5 \pm 76.4$
PT DL	$0.12 \pm 0.01$	$0.13 \pm 0.03$	$0.12 \pm 0.03$	$0.10 \pm 0.02$	$0.11 \pm 0.11$	$0.05 \pm 0.03$	$0.18 \pm 0.11$	$0.11 \pm 0.06$	$0.19 \pm 0.17$	$0.71 \pm 0.41$
KD Ch	$3.80 \pm 0.95$	$2.64 \pm 1.90$	$2.16 \pm 1.29$	$3.22 \pm 1.03$	$3.00 \pm 0.38$	$3.74 \pm 1.29$	$4.20 \pm 3.54$	$1.27 \pm 1.01$	$4.90 \pm 4.24$	$10.2 \pm 0.94$
20	$10.4 \pm 14.0$	0.24 ± 4.55	7.43 ± 2.08	$9.48 \pm 8.15$	$3.34 \pm 1.03$	$17.0 \pm 21.0$	$3.08 \pm 4.70$	4.50 ± 3.02	$8.32 \pm 10.7$	$9.05 \pm 10.0$
SC			10D							$12.3 \pm 13.2$
Sill	$0.10 \pm 0.01$	$0.11 \pm 0.01$	$0.11 \pm 0.05$ 7 10 + 2 40	$0.09 \pm 0.02$	$0.08 \pm 0.01$ 8.75 $\pm 0.48$	ND 949   416	252   252	104   226	$0.04 \pm 0.02$	$0.41 \pm 0.22$
511	$03.7 \pm 42.7$ 7 42 + 1 59	20.7 ± 29.4	$7.19 \pm 2.49$	$10.2 \pm 12.7$	$0.75 \pm 0.40$	$64.0 \pm 41.0$	55.2 ± 55.5	$10.4 \pm 5.20$	$21.9 \pm 10.1$	$22.0 \pm 13.0$
31 To	$7.45 \pm 1.56$	$115 \pm 0.12$	100	$117 \pm 0.19$	$7.36 \pm 0.32$	1 10   0 22	1 20 L 0 22	ND 426 ± 0.11	ND 451 + 0.60	42.9 ± 27.0
Ti	$348 \pm 766$	$1.15 \pm 0.15$	$1.22 \pm 0.10$ $27.1 \pm 7.87$	$1.17 \pm 0.10$ $32.2 \pm 15.0$	100	$1.15 \pm 0.52$ $07.7 \pm 34.1$	$4.25 \pm 0.52$ 131 $\pm 50.8$	$4.50 \pm 0.11$ $74.2 \pm 21.6$	$4.51 \pm 0.00$ 176 $\pm 115$	/12 ± 318
T1	$0.51 \pm 0.25$	$0.49 \pm 0.30$	$27.1 \pm 7.07$ 0.58 $\pm$ 0.15	$0.56 \pm 0.32$	$40.1 \pm 12.3$	$0.12 \pm 0.20$	$151 \pm 50.8$	$74.2 \pm 21.0$ 0.74 $\pm$ 0.20	$170 \pm 113$ 0.76 ± 0.20	$413 \pm 310$ 0.53 $\pm 004$
II	$0.31 \pm 0.23$ 0.34 + 0.08	$0.45 \pm 0.05$	$0.35 \pm 0.15$	$0.30 \pm 0.32$ 0.36 + 0.12	$0.31 \pm 0.27$ $0.28 \pm 0.05$	$0.42 \pm 0.23$	$0.55 \pm 0.50$	ND	ND = 0.23	$1.44 \pm 0.90$
v	$5.84 \pm 3.08$	$5.50 \pm 0.05$	ND	$9.30 \pm 0.12$ $9.42 \pm 4.91$	$413 \pm 335$	$531 \pm 337$	$5.87 \pm 5.65$	ND	$12.4 \pm 6.75$	$1.44 \pm 0.50$ $166 \pm 168$
Ŵ	$0.72 \pm 0.46$	632 + 330	$2.45 \pm 0.66$	$1.91 \pm 1.91$	$1.49 \pm 0.27$	$0.93 \pm 0.69$	$307 \pm 205$	$351 \pm 0.83$	$727 \pm 670$	$13.4 \pm 11.8$
Y	$1.12 \pm 0.31$	$0.56 \pm 0.41$	$0.85 \pm 0.37$	$0.99 \pm 0.74$	$0.71 \pm 0.20$	ND	ND	ND	$0.17 \pm 0.17$	$0.57 \pm 0.30$
Yb	$0.10 \pm 0.02$	$0.05 \pm 0.03$	$0.06 \pm 0.04$	$0.08 \pm 0.05$	$0.05 \pm 0.03$	ND	ND	ND	ND	$0.12 \pm 0.04$
Zr	$5.86 \pm 1.84$	$9.08 \pm 0.95$	$8.06 \pm 1.71$	$8.13 \pm 3.17$	$7.10 \pm 0.47$	ND	ND	ND	ND	42.4 + 21.3

Levels in ng/m<sup>3</sup>. ND: Not detected. Be, Hf, Ho, Nb, P, Se, Ta, Tb, and Th were not detected in any sample.

In TSP samples, Ba, Be, Dy, Er, Eu, Gd, Ge, Hf, Ho, Mg, Mo, Nb, Sc, Se, Sr, Ta, Tb, Th, U, Yb, and Zr were not detected at any site, while K and V were not found in E3. Moreover, Hg was detected only in E2, while P and Sm were found only in E4. Sodium ranged between 11,261  $\pm$ 1070 ng/m<sup>3</sup> at E1 and 14,676  $\pm$  1430 ng/m<sup>3</sup> at E2, Ca ranged from 5242  $\pm$  844 ng/m<sup>3</sup> at E1 to 8641  $\pm$  1829 ng/m<sup>3</sup> at E4, Fe ranged from 1111  $\pm$  320 ng/m³ at E3 to 1564  $\pm$  546 ng/m³ at E4, K ranged from not detected in E3 to 1560  $\pm$  408 ng/m<sup>3</sup> in E1, while Al ranged from  $665 \pm 402 \text{ ng/m}^3$  in E3 to  $2641 \pm 1194 \text{ ng/m}^3$  at E4. This sampling point, E4, exhibited the highest level of main elements among the 4 sampling sites, which could be due to the higher dust resuspension from the larger area of cultivated land. The trace elements in TSP from the e-waste recycling region were dominated by Cu, Pb, and Ti at the four sampling sites, with the exception of Ni with a higher level than Ti at E1. Comparing trace elements in TSP, significant differences (*p* < 0.05) were found for Ca, Ce, Cr, K, La, Na, Nd, Ni, Pr, Sm, Sr, and Y, all of them presented higher levels in BG area than in e-waste area. Some elements that shown the reverse trend, higher TSP levels in e-waste parks than background area were Cu (442 vs. 284 ng/m<sup>3</sup>), Pb (142 vs. 89.5 ng/m<sup>3</sup>), Sn (38.1 vs. 22.6 ng/m<sup>3</sup>), Te (3.59 ng/m<sup>3</sup> vs. ND), and Tl (0.61 vs. 0.53 ng/m<sup>3</sup>). In PM<sub>2.5</sub>, Higher levels of Cr (9.55 vs. 39.1 ng/m<sup>3</sup>), Eu (0.04 vs. 0.10 ng/m<sup>3</sup>), and Sr (1.90 vs. 7.58 ng/m<sup>3</sup>) were found in BG area while higher levels of Cu (162 vs. 32.4 ng/m<sup>3</sup>) and Te (0.90 ng/m<sup>3</sup> vs. ND) were noted in e-waste recycling parks.

Cu and Pb were the most abundant trace elements detected in  $PM_{2.5}$ in the study areas, which is consistent with the presence of Cu, Pb, and Sn in electronic components such as diodes, audios, CD capacitances, electrical resistances and polypropylene film capacitances (Ruan et al., 2017). In turn, Sn was detected in both TSP and PM<sub>2.5</sub> in all sampling sites, with the mean concentration of Sn in particles at E1 being even higher than that of Ti. Moreover, Mn at E2, E3 and E4 presented a relatively high concentration. A study of 15 heavy metals in airborne sizefractionated particles in the same region was conducted by Huang et al. (2016) in 2012. It was found that Pb, Ti, Cu, and Mn were the dominating trace elements, which is in agreement with the results of our study. Furthermore, TSP levels of Pb and Ti in both studies were comparable (160 vs. 142 ng/m<sup>3</sup> for Pb and 140 vs. 120 ng/m<sup>3</sup> for Ti); while Cu levels increased (90 vs. 442 ng/m<sup>3</sup> in 2012 vs. present study, respectively) and levels of Mn decreased (73 vs. 49.0 ng/m<sup>3</sup> in 2012 vs. present study, respectively). Bi et al. (2010) reported that, in 2007, the dominant trace elements in particles emitted from recycling of waste printed circuit boards in Guiyu were Pb, Sn, Cu and Ti, with the levels of Pb (average =  $4.42 \,\mu g/m^3$ ) and Sn (average =  $2.09 \,\mu g/m^3$ ) being dramatically higher than those found in the current survey. Gangwar et al. (2019) analyzed the concentrations of various heavy metals (Pb, Cu, Zn, Ni and Cr) contained in PM<sub>10</sub> from an illegal e-waste recycling region in India. The levels of all metals –except for Zn- were 1 or 2 orders of magnitude higher than our results in TSP. Overall, Pb, Cu and Ti were still the most dominating trace elements in particles emitted during transition of e-waste recycling activities in the region under current evaluation.

Copper is a representative element emitted from e-waste recycling activities (Robinson, 2009). In present work also higher Cu levels around e-waste facilities than BG site were reported in both TSP and PM<sub>2.5</sub>. For exploring the possible element indicators of e-waste recycling activity, Pearson's correlations of Cu with other trace elements were performed in each sampling site. Significant (p < 0.05) positive correlations between Cu and Cs ( $r^2 = 0.790$ , p = 0.03), and between Cu and Tl ( $r^2 = 0.790$ , p = 0.03) were found in PM<sub>2.5</sub> in E1. Copper in PM<sub>2.5</sub> in E2 exhibited significant positive correlations with Ge, Pb, Tl, V  $(r^2 = 0.771-0.886)$ , at p < 0.05 and W  $(r^2 = 0.935)$  at p < 0.01. Moreover, in PM<sub>2.5</sub> there were significant positive correlations between Cu and Cd, Ce, Mn, Sn  $(r^2 = 0.721-0.851)$  at p < 0.05, while Te  $(r^2 =$ 0.899) and W ( $r^2 = 0.968$ ) at p < 0.01 in E4. In TSP, significant positive correlations with Cu was found for Co, Cs and W ( $r^2 = 0.714-0.766$ , p < 0.05) in E1, W ( $r^2 = 0.954$ , p < 0.01) in E2, as well as Ni ( $r^2 = 0.717$ , p = 0.03), Te ( $r^2 = 0.798$ , p = 0.04) and W ( $r^2 = 0.987$ , p < 0.001) in E4. There were no significant correlations between Cu and other trace elements in E3, neither in PM<sub>2.5</sub> nor in TSP. Significant positive correlations between Cu and different trace elements were found in different ewaste recycling parks implying different recycled e-waste products, or different disassembly methods. Interestingly, W was the only trace element showing significant positive correlations with Cu, in both fine particles (in E2 and E4) and coarse particles (in E1, E2 and E4). It has been reported that the W-Cu composite is a promising material for electronic packaging and heat sink, being also an ideal application for electrical contacts because of their excellent performance (Dong et al., 2018). It should take into account that with a large amount of statistical tests, sometimes, might give false positive findings.

## 3.1.3. Carbonaceous matters, water-soluble ions

Concentrations of OC, EC, sum of OC and EC, water-soluble ions (Cl<sup>-</sup>,  $SO_4^{2-}$ ,  $NH_4^+$  and  $NO_3^-$ ) in PM<sub>2.5</sub> and TSP are summarized in Table 2. EC generally comes from the incomplete combustion of fossil and biomass fuel, while OC can be directly discharged as primary OC, or generated by atmospheric reactions (Zhang et al., 2016). There were significant differences (p < 0.05) in OC levels between E2 and E3 in PM<sub>2.5</sub>, and between E3 and E4 in TSP. However, no significant differences (p > 0.05)

of EC in PM<sub>2.5</sub> and TSP were found between sampling sites. In addition, no significant (p > 0.05) differences were found in OC and EC between BG and e-waste recycling parks. As it can be seen in Table 2, the highest concentrations of  $Cl^{-}$  and  $SO_{4}^{2-}$  in both  $PM_{25}$  and TSP were detected in E4, while the highest levels of  $NH_4^+$  and  $NO_3^-$  in these particles were found in E2. The levels of water-soluble ions in the rural e-waste recycling region showed the same order in all sampling sites:  $NO_3^ > NH_4^+ > SO_4^2 > Cl^-$ . Comparing with the results of PM<sub>2.5</sub> from our previous study (Ding et al., 2018), the levels of NH<sub>4</sub><sup>+</sup> in this region were relatively constant (5.14 vs. 3.96 µg/m<sup>3</sup>, in 2013-2014 vs. present, respectively), while those of  $Cl^{-}$  (1.46 vs. 0.32 µg/m<sup>3</sup>) and  $SO_4^{2-}$  (13.4 vs. 2.20  $\mu$ g/m<sup>3</sup>) showed a decreasing trend after introduction of new local policy (Liu, 2015). However, concentrations of NO<sub>3</sub><sup>-</sup> in this area were more than twice higher than those found in 2013 by Ding et al. (2018) (4.09 vs. 10.9 µg/m<sup>3</sup>, in 2013–2014 vs. present, respectively). Tian et al. (2017), reported that the decrease of  $SO_4^{2-}$  and the increase of  $NO_3^-$  in airborne particles of Chongging, was probably the result of the performance of desulfurization projects, as well as the elevated number of vehicles. The increase in vehicles traffic in the study area could be responsible for the increase of  $NO_3^-$  levels. However, in TSP or in PM<sub>2.5</sub>, no significant differences (p > 0.05) were noted in carbonaceous fraction or soluble ions, between BG site and e-waste recycling parks, except for the higher levels of NH4<sup>+</sup> in TSP, in e waste parks  $(8.37 \text{ vs.} 1.14 \mu\text{g/m}^3).$ 

Significant correlations between NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> (r<sup>2</sup> = 0.673, p < 0.001) and SO<sub>4</sub><sup>2-</sup> (r<sup>2</sup> = 0.386, p = 0.002) were observed, while no significant correlations were found between NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup> in PM<sub>2.5</sub>. A strong correlation between NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> means more formation of NH<sub>4</sub>NO<sub>3</sub> rather than (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>HSO<sub>4</sub> in PM<sub>2.5</sub>. Even more significant correlations between NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> (r<sup>2</sup> = 0.930, p < 0.001), SO<sub>4</sub><sup>2-</sup> (r<sup>2</sup> = 0.411, p = 0.001) and Cl<sup>-</sup> (r<sup>2</sup> = 0.290, p < 0.008) were found in TSP. These results suggest that, at present, NH<sub>4</sub>NO<sub>3</sub> is the dominating formation of ions in particles from rural e-waste recycling regions. Generally, ammonia first neutralizes sulphuric acid to ammonium bisulphate and ammonium nitrate (Liu et al., 2017). However, the formation of secondary inorganic ions intensively depends on the atmospheric conditions and availability of its precursors (Xu et al., 2017).

### 3.1.4. Composition of particles

The main components (mineral matter, sea spray, OM + EC, SIA, trace elements and unaccounted) of  $PM_{2.5}$  and TSP samples, collected from a rural e-waste recycling region, are depicted in Fig. 3. For  $PM_{2.5}$ , mineral matter was the most abundant component in almost all sampling sites, except for E2. SIA was the most abundant in E2, followed by OM + EC, which would indicate a larger contribution of

Table 2

Levels of organic carbon (OC), elemental carbon (EC), ions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) and indirect determinations (OM, CO<sub>3</sub><sup>2-</sup>, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) in PM<sub>2.5</sub> and TSP samples collected near four e-waste recycling parks (E1, E2, E3, E4) and a background area (BG) in 2016.

	PM <sub>2.5</sub>					TSP				
	E1 (n = 5)	E2 (n = 5)	E3 (n = 5)	E4 (n = 5)	BG (n = 2)	E1 (n = 5)	E2 (n = 5)	E3 (n = 5)	E4 (n = 5)	BG (n = 2)
OC	$8.33 \pm 1.68$	$10.9\pm3.57$	$5.76 \pm 1.20$	$9.18 \pm 4.56$	$5.13 \pm 0.73$	$12.0\pm1.63$	$15.1\pm3.90$	$9.21 \pm 1.37$	$15.6\pm5.89$	$14.2\pm1.22$
EC	$2.81\pm0.45$	$3.08 \pm 1.03$	$1.85\pm0.18$	$3.17 \pm 1.86$	$2.54\pm0.52$	$3.68 \pm 1.02$	$3.80 \pm 1.77$	$2.25\pm0.25$	$4.63\pm3.07$	$4.56\pm0.71$
OC + EC	$11.1 \pm 1.92$	$14.0\pm4.49$	$7.62 \pm 1.16$	$12.4\pm6.32$	$7.67 \pm 1.25$	$15.6\pm2.48$	$18.9\pm5.53$	$11.5 \pm 1.53$	$20.2\pm8.64$	$18.7\pm1.93$
OM	$13.3\pm2.69$	$17.5\pm5.71$	$9.22 \pm 1.93$	$14.7\pm7.29$	$8.21 \pm 1.16$	$19.1\pm2.61$	$24.2\pm6.24$	$14.7\pm2.19$	$24.9\pm9.43$	$22.6 \pm 1.95$
$CO_{3}^{2-}$	$6.97\pm0.73$	$7.29 \pm 1.22$	$7.80 \pm 1.19$	$8.62 \pm 2.83$	$6.02\pm0.59$	$7.94 \pm 1.27$	$8.64 \pm 2.03$	$8.20\pm1.40$	$13.0\pm2.74$	$31.7 \pm 17.9$
SiO <sub>2</sub>	$5.19 \pm 1.93$	$3.52\pm3.65$	$4.45\pm2.49$	$4.77 \pm 3.69$	$3.21 \pm 1.91$	$8.73 \pm 2.43$	$7.18\pm5.31$	$3.77\pm2.28$	$15.0\pm6.77$	$20.5 \pm 15.1$
$Al_2O_3$	$1.73\pm0.64$	$1.17 \pm 1.21$	$1.43\pm0.83$	$1.59 \pm 1.23$	$1.07\pm0.64$	$2.91\pm0.81$	$2.39 \pm 1.77$	$1.26\pm0.76$	$4.99 \pm 2.26$	$6.84 \pm 5.05$
Cl <sup>-</sup>	$0.34\pm0.27$	$0.26\pm0.07$	$0.20\pm0.01$	$0.50\pm0.46$	$0.13\pm0.15$	$0.27\pm0.21$	$0.53\pm0.08$	$0.43\pm0.02$	$0.73\pm0.30$	$0.69\pm0.38$
$SO_{4}^{2-}$	$1.02\pm0.39$	$3.05\pm3.07$	$0.79\pm0.03$	$3.96 \pm 3.89$	$0.59\pm0.53$	$0.95\pm0.46$	$2.89 \pm 1.62$	$1.80\pm0.13$	$5.32\pm3.80$	$2.27 \pm 2.23$
$NH_4^+$	$1.86\pm0.70$	$5.85 \pm 2.69$	$4.04 \pm 1.18$	$4.10 \pm 2.69$	$1.25\pm0.51$	$3.47 \pm 1.35$	$11.4\pm4.85$	$9.15 \pm 2.71$	$9.45 \pm 4.97$	$1.14\pm0.76$
$NO_3^-$	$4.95\pm2.12$	$15.2\pm5.59$	$12.5\pm3.79$	$11.0\pm6.18$	$4.54\pm0.92$	$6.67 \pm 1.94$	$16.3\pm6.79$	$13.1\pm3.52$	$14.0\pm4.38$	$10.2\pm9.56$

Levels in  $\mu g/m^3$ . OC + EC: organic carbon plus elemental carbon. OM: organic matter.



Fig. 3. Main components of collected  $PM_{2.5}$  and TSP around the four e-waste recycling sites and a background area. Results are expressed as percentage of the mass.

anthropogenic activities to form PM<sub>2.5</sub>. The composition of TSP in E2 presented similar components with PM<sub>2.5</sub>, which were dominated by SIA. SIA was also the most abundant component in TSP from E3, while mineral matter showed the highest percentage in TSP from E1 and E4. Mineral matter was the most abundant component in both TSP and PM<sub>2.5</sub> in BG, with the percentages being higher than those found at all e-waste recycling sites. The percentages of sea spray in BG were higher than those in the e-waste recycling region. The trace element component contributed the lowest to total particle mass. Overall, mineral matter (21.7–36.7% in PM<sub>2.5</sub> and 16.6–31.6% in TSP), OM + EC (18.9–27.8% in PM2.5 and 18.7-24.1% in TSP) and SIA (14.1-29.1% in PM2.5 and 11.6-26.0% in TSP), all together are the dominating components in particles in this rural e-waste recycling region. Comparing composition of TSP between BG area and all together the four e-waste areas, higher (p < 0.05) contribution levels (in %) of mineral mater and sea spray were registered in BG, while lower (p < 0.05) contribution were found in secondary inorganic aerosol. By contrast, in PM<sub>2.5</sub>, no significant differences (p > 0.05) were found between BG and all e waste sites considered together. Although, some significant differences (p < 0.05) were detected in PM<sub>2.5</sub> composition between BG and e waste individual areas (between E2 and BG in mineral matter; and between E2, E3, and E4 and BG in trace elements). Results here presented were in the same line with the results we have recently obtained near a cement plant in Catalonia, Spain (Rovira et al., 2018; Sánchez-Soberón et al., 2015). However, mineral matter generally presented the highest percentage in particles from this e-waste recycling region, while OM + EC was the most abundant component in airborne particles collected near the cement plants. The possible reasons of the difference were the larger cultivated area in this rural area and less thermal process during e-waste recycling. Principal components analysis (PCA) were performed with main components of TSP and PM<sub>2.5</sub> (Fig. 4). A pair of two-dimension model was created one for TSP and other for PM<sub>2.5</sub>, explaining 67% and 81% of the data variance. In TSP model, first



Fig. 4. Principal component analysis of main components of TPS and PM<sub>2.5</sub> collected in four e-waste recycling parks (from E1 to E4) and background site (BG).

component was positively associated with mineral material, trace elements and negatively correlated with secondary inorganic aerosol while the second component was correlated positively with organic matter and elemental carbon and negatively with sea spray. One the other hand, for PM<sub>2.5</sub> first component was correlated positively with mineral material and sea spray, and negatively correlated with secondary inorganic aerosol. Regarding second component was positively correlated with Trace elements and organic matter and elemental carbon. As can be observed BG sites were cluster together in the PCA of TSP and distanced from e-waste recycling parks, that appears grouped by site specially the E3. For PM<sub>2.5</sub>, BG sites also appeared grouped but this time with E1 and differentiated from other e-waste recycling parks (E2, E3 and E4).

# 3.2. Exposure model and human health risks assessment

The estimated concentrations of indoor  $PM_{2.5}$  using IAQX software and exposures are shown in Table 3. E2 and E4 presented the highest exposure values  $(1.4 \cdot 10^{-2} \text{ and } 1.2 \cdot 10^{-2} \text{ mg/(kg·day)})$ , respectively. Working and leisure time contributed the most to exposure in all sampling sites. Exposures to toxic elements (As, Cd, Cr, Co, Mn, Ni, Pb, U, and V) at each sampling site are depicted in Fig. 5. The highest exposure by inhalation corresponded to Pb at each sampling site. In general terms, exposure values in this e-waste recycling region were ordered as

#### Table 3

Outdoor and indoor (modeled with IAQX software) PM<sub>2.5</sub> concentrations and exposure levels in e-waste recycling sites (E1 to E4) and a background area (BG).

	Concentration (µg/m <sup>3</sup> )		Exposure (	Sum		
	Outdoor	Indoor	Sleeping	Work/Leisure	Outdoor	
E1	42.8	17.8	6.8E-04	5.0E-03	2.3E-03	8.0E-03
E2	75.5	30.3	1.2E-03	8.5E-03	4.0E-03	1.4E-02
E3	46.6	18.7	7.2E-04	5.3E-03	2.5E-03	8.5E-03
E4	66.0	26.5	1.0E-03	7.5E-03	3.5E-03	1.2E - 02
BG	37.8	15.2	5.8E-04	4.3E-03	2.0E-03	6.9E - 03

follows: Pb > Mn > As > V > Cd > U > Co. Moreover, exposure to Ni at E1 was the second in importance among all harmful elements, followed by Cr, Mn, As, V, Cd, Co and U.

Regarding non-carcinogenic risks, HQ for all chemicals was below the safety threshold, which was set as 1. Arsenic presented the highest HQ values (from 0.22 in E4 to 0.39 in E1, with a median of 0.32). However, Ni at E1 showed an extraordinary high HQ 0.46. In turn, Mn also exhibited high HQ levels, ranging from 0.17 for E3 to 0.23 for E2 (median = 0.21). The values of HQ for the rest of elements were all lower than 10% of the threshold, 1. In contrast, HQ in the background area was as high as in the e-waste recycling region, with HQ values of 0.39, 0.26 and 0.19 for Ni, Mn and As, respectively. Carcinogenic risks are shown in Table 4. Arsenic and Cd in PM<sub>2.5</sub> in the four e-waste sampling sites, and Cr (VI) and Ni in PM<sub>2.5</sub> in E1 presented carcinogenic risks higher than  $10^{-6}$ . Carcinogenic risks of As, Cr (VI) and Ni in BG were also higher than  $10^{-6}$ . According to the US EPA (2002) acceptable cancer



Fig. 5. Inhalation exposure to toxic elements contained in  $PM_{2.5}$  from e-waste recycling parks (E1 to E4) and a background area (BG).

## Table 4

Cancer risks due to exposure to trace elements associated to  $PM_{2.5}$  in e-waste recycling parks (E1 to E4) and a background area.

	As	Ве	Cd	Со	Cr (VI)	Ni	Pb
E1	1.1E-05	NC	1.4E-06	7.4E-07	3.9E-05	4.6E-06	2.8E-07
E2	9.8E-06	NC	1.1E - 06	4.9E - 07	NC	5.2E-07	2.1E-07
E3	7.5E-06	NC	1.3E-06	4.3E-07	NC	5.1E - 07	1.9E-07
E4	6.0E-06	NC	1.1E - 06	4.6E - 07	NC	6.2E - 07	1.8E-07
BG	5.4E-06	NC	9.1E-07	7.1E-07	5.4E-05	6.5E-06	6.8E-08

NC: not calculated due to air levels being below detection limits. Acceptable cancer risk is below  $10^{-6}$  (US EPA, 2002).

risk is below  $10^{-6}$ . Furthermore, As in E1 and Cr (VI) in E1 and BG were even higher than  $10^{-5}$ . Although cancer values are flexible  $(10^{-6}-10^{-4})$  depending on the variable characteristics of each individual (US EPA, 1996), the high cancer risks in E1 clearly are of concern. Arsenic may not be released from e-waste recycling activities as no correlation between As and Cu was found at any sampling site. It could come from soil resuspension taking into account that the use of pesticides and herbicides in agriculture activities in this rural region is quite important (De La Cruz et al., 2018). Furthermore, although the highest carcinogenic risk (due to As) may be not directly derived from e-waste recycling activities, inhabitants living near the e-waste recycling park are still subject to high carcinogenic risks from Cd, Co and Pb emitted from e-waste recycling activities. In addition, it should be taken into account that usually to assess exposure and the human health risk, PM<sub>10</sub> are considered but in present study, we estimated the human health risk with PM<sub>2.5</sub>. Therefore, higher risk levels would be expected if risks were calculated using the levels of trace elements in PM<sub>10</sub>.

## 4. Conclusions

TSP and PM<sub>2.5</sub> samples were collected near four e-waste recycling parks during the transition from extensive e-waste dismantling methods to advanced dismantling methods, in an e-waste recycling region of Southern China. Concentrations and compositions were analyzed to identify the characteristics of particles released from e-waste recycling activities. Moreover, effects of PM<sub>2.5</sub> to individuals living in the neighborhood were also evaluated. Levels of TSP and PM<sub>2.5</sub> were lower with advanced recycling methods than with small recycling ewaste workshops operating in the sampling region. Higher levels of Cu Pb, Sn, Te, and Te in TPS were found in e-waste parks than BG, from these only Cu and Te remained significantly higher in PM<sub>2.5</sub>. Significant high positive correlations between Cu and both W and Te were found. These elements are present and can be released from electrical and electronical components during e-waste recycle processes, which may be the characteristic component in airborne particles from the current study region after 2015. Non-carcinogenic risks in all sites were lower than the threshold (HQ < 1), with As being the element presenting the highest HQ value in the study area. Carcinogenic risks of As and Cd in all sites, as well as Ni, Cr in E1, were higher than  $10^{-6}$ , which is considered as the acceptable limit according to the US EPA. Carcinogenic risks of As and Cr in E1 were even higher than  $10^{-5}$ . Consequently, people living near these e-waste recycling parks would be subjected to high carcinogenic risks. However these risk cannot be attributable only to e-waste recycling parks but also to traffic and other activities which also indicate a high carcinogenic risk in BG sites.

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