1 **Characterization and risk assessment of total suspended particles (TSP) and fine**
2 **particles (PM$_{2.5}$) in a rural transformational e-waste recycling region of Southern**
3 **China.**

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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 ($>10^{-5}$).

1. Introduction

Air pollution has become a global environmental problem in low, middle and high-income countries. Around 4.2 millions 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 $PM_{2.5}$ 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 e-waste 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

96 iii) to evaluate the potential risks for human health due to exposure to toxic elements

97 contained on fine particles ($PM_{2.5}$).

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99 **2. Materials and methods**

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101 *2.1 Sites description and sampling*

102 TSP and $PM_{2.5}$ were collected around four e-waste recycling parks (E1, E2, E3 and

103 E4) in a rural region of Qingyuan, southern China, in October-November of 2016

104 (Figure 1). This region is one of the biggest recycling e-waste sites in China, where

105 e-waste recycling activities have been conducted for more than 30 years (Xiao et al.,

106 2014). However, with the introduction of new local policy, scatter e-waste dismantling

107 workshops were replaced by formal dismantling parks from 2015 (Liu, 2015).

108 Samplers were placed on the roof (10 m above the ground), near (between 270 and

109 800 m), and downwind of the e-waste recycling parks. The background site (BG) was

110 located at an adjacent rural region which at the southeast and 20 kilometers far away

111 from the sampling region. There is no significant industrial activity around

112 background site. Samples in background sites were collected, when the winds

113 direction was blowing from southeast.

114 In each sampling site, 24-h samples of TSP and $PM_{2.5}$ were collected on quartz

115 fibber filters (QFFs) during five consecutive days (n=5), except in BG site where only

116 two samples were collected. The QFFs were pre-treated at 450 °C for 4 hours, and

117 conditioned at 25 °C and 40% relative humidity for 24 hours. Two high-volume active

samplers were used to collect samples simultaneously in each site, one for $PM_{2.5}$ at a

flow of 1.13 m^3/min (TE-6001, Tish Environment Inc., Ohio, USA) and another for

TSP, at a flow of 0.28 m^3/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 hours 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^2) 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

3mL of hydrofluoric acid (Suprapur, E. Merck, Darmstadt, Germany) in Teflon

vessels. After 8 hours at room temperature, and 8 hours 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

140   elements (Al, As, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, La,

141   Li, Hg, Mn, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sr, Tb, Th, Ti, Tl, U, V, W, Y, Yb, and Zr)

142   were analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Perkin

143   Elmer Elan 6000), while Ba, Ca, Fe, K, Mg and Na were analyzed by inductively

144   coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer Optima

145   3200RL).

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147   *2.4 Ions*

148   A portion of the filter was disposed to analyze ions. Filters were extracted with 15

149   mL of ultrapure water through axial agitation for 12 hours and sonicated at 60°C for

150   10 minutes. The mixtures were filtered with a 0.47 μm membrane filter. The

151   concentrations of Cl^-, SO_4^{2-}, and NO_3^- were determined by ion chromatograph

152   (Dionex D-300), while those of NH_4^+ were determined by the reaction of Berthelot.

153   Furthermore, the levels of CO_3^{2-} and SiO_2 were calculated from stoichiometric ratios,

154   which are $CO_3^{2-} = 1.5Ca + 2.5Mg$ and $2Al_2O_3 = SiO_2$. In turn, all of the aluminium

155   was assumed to be present in oxide form.

156

157   *2.5 Particle characterization*

158   Particle matter (PM) was divided into six main components: mineral matter (sum of

159   CO_3^{2-}, SiO_2, Al_2O_3, Ti, P, Mn, Mg, K, Fe and Ca), sea spray (sum of Na^+ and Cl^-), OM

160   + EC, secondary inorganic aerosols (sum of SO_4^{2-}, NH_4^+ and NO_3^-), trace elements

161   (sum of the rest of elements), and unaccounted (the difference between the PM

162 concentration and the sum of the rest of fractions).

163

164 *2.6 Quality assurance and Quality control (QA/QC)*

165 Field blanks, procedural blanks, duplicate samples and standards (Standard

166 Reference Material 1648a Urban Particulate, National Institute of Standards and

167 Technology and Standard sucrose solution, Merck, Darmstadt, Germany) were used

168 for quality assurance and quality control. The detection limits (DLs) of OC and EC

169 were 0.11 μg C/m^3 and 0.05 μg C/m^3, respectively. The DLs of trace elements were

170 0.06 ng/m^3 for Ce, Cs, Dy, Er, Eu, Gd, Ho, La, Nd, Pr, Sm, Tb, Th, Tl, U, Y and Yb;

171 0.12 ng/m^3 for Ba, Bi, Cd, Co, Li, Nb, Pb, Rb, Sb, Sr, Ta, Te and W; 0.24 ng/m^3 for

172 Hg and Mn; 0.59 ng/m^3 for Be, Cu, and Sn; 1.18 ng/m^3 for As, Ge, Hf, Ni, Ti, and Zr;

173 2.35 ng/m^3 for Cr, Mo and Zn, 3.53 ng/m^3 for Sc and V; 5.88 ng/m^3 for Se; 11.8 ng/m^3

174 for Fe; 58.8 ng/m^3 for Al, B, Ca and Mg; 588 ng/m^3 for K, P; 1176 ng/m^3 for Na.

175 Finally, the DLs of ions were: 0.04 μg/m^3 for Cl$^-$, 0.08 μg/m^3 for NO$_3^-$, 0.20 μg/m^3 for

176 SO$_4^{2-}$ and 0.008 μg/m^3 for NH$_4^+$. The concentrations of samples whose values were

177 below the respective DL were considered as one-half of that limit (ND = $^1/_2$ DL).

178

179 *2.7 Human exposure and health risks assessment*

180 The calculations for human exposure and health risks assessment have been

181 described in recent studies (Rovira et al., 2010; Sánchez-Soberón et al., 2015). Briefly,

182 exposure was estimated by considering only the inhalation route for an average adult

183 in a mean daily routine. Equation 1 was used for evaluating exposure, being expressed

as:

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

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^3, 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^3/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 hours/day (Idescat, 2012). Body weight (BW) was set at 70 kg.

Three equations (2) – (4) were used for assessing human health risks:

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

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

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

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 ($PM_{2.5}$ 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 = ½ 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 $PM_{2.5}$

3.1.1 Levels of TSP and $PM_{2.5}$

Levels of TSP and $PM_{2.5}$ in the four e-waste recycling parks and background area are depicted in Figure 2. Concetrations of TSP ranged from 90.8 ± 15.5 μg/m^3 at E3 to 137 ± 53.2 μg/m^3 at E4, while $PM_{2.5}$ levels ranged from 42.8 ± 4.93 μg/m^3 at E1 to

226   75.5 ± 29.4 μg/m^3 at E2. Regarding TSP, significant ($p<0.05$) differences were noted

227   between background area (BG) (168 μg/m^3) and two e-waste recycling parks (E1

228   (94.5 μg/m^3) and E3 (90.8 μg/m^3)), however not significant ($p>0.05$) differences were

229   detected in PM$_{2.5}$ levels between background area than e-waste recycling parks

230   (considered individually or all together). According to Chinese legislation (GB 3095 –

231   2012) daily limits for PM$_{2.5}$ and TSP are set at 75 μg/m^3 and 300 μg/m^3, respectively.

232   This means that the daily concentrations of PM$_{2.5}$ frequently exceeded the limits in E2

233   and E4. In addition, PM$_{2.5}$ levels were much higher than the threshold values of the

234   World Health organization (WHO) (10 and 25 μg/m^3 for annual and daily means,

235   respectively) and those of the European Union (25 μg/m^3 for annual mean). The

236   average PM$_{2.5}$ concentration between 2013 and 2014, measured by Ding et al. (2018)

237   in the same region, when informal e-waste workshops were operating, was 182 ± 62.0

238   μg/m^3, twice higher than that found in the present study. Comparing with data from

239   other e-waste recycling regions, the concentrations of PM$_{2.5}$ in Guiyu in 2017 (mean

240   level = 39.1 μg/m^3) were lower than those found in the current survey (Zhang et al.,

241   2019), while the levels of PM$_{10}$ between 193 to 243 μg/m^3 were recently reported

242   from illegal e-waste burning regions in India (Gangwar et al., 2019).

243

244   3.1.2 Mineral and trace elements

245   Table 1 shows the concentrations of trace elements in both PM$_{2.5}$ and TSP. In PM$_{2.5}$

246   samples, Be, Hf, Hg, Ho, Nb, P, Sc, Se, Ta, Tb and Th levels were not detected in any

247   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.

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 11261 ± 1070 ng/m^3 at E1 and 14676 ± 1430 ng/m^3 at E2, Ca ranged from 5242 ± 844 ng/m^3 at E1 to 8641 ± 1829 ng/m^3 at E4, Fe ranged from 1111 ± 320 ng/m^3 at E3 to 1564 ± 546 ng/m^3 at E4, K ranged from not detected in E3 to 1560 ± 408 ng/m^3 in E1, while Al ranged from 665 ± 402 ng/m^3 in E3 to 2641 ± 1194 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^3), Pb (142 vs. 89.5 ng/m^3), Sn (38.1 vs. 22.6 ng/m^3), Te (3.59 ng/m^3 vs. ND), and Tl (0.61 vs. 0.53 ng/m^3).

In PM$_{2.5}$, Higher levels of Cr (9.55 vs. 39.1 ng/m^3), Eu (0.04 vs. 0.10 ng/m^3), and Sr (1.90 vs. 7.58 ng/m^3) were found in BG area while higher levels of Cu (162 vs. 32.4 ng/m^3) and Te (0.90 ng/m^3 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$_{2.5}$ 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 size-fractionated 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^3 for Pb and 140 vs. 120 ng/m^3 for Ti); while Cu levels increased (90 vs. 442 ng/m^3 in 2012 vs. present study, respectively) and levels of Mn decreased (73 vs. 49.0 ng/m^3 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 µg/m^3) and Sn (average = 2.09 µg/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$_{10}$ from an illegal e-waste recycling region in India. The levels of all

292 metals –except for Zn- were 1 or 2 orders of magnitude higher than our results in TSP.

293 Overall, Pb, Cu and Ti were still the most dominating trace elements in particles

294 emitted during transition of e-waste recycling activities in the region under current

295 evaluation.

296 Copper is a representative element emitted from e-waste recycling activities

297 (Robinson, 2009). In present work also higher Cu levels around e-waste facilities than

298 BG site were reported in both TSP and $PM_{2.5}$. For exploring the possible element

299 indicators of e-waste recycling activity, Pearson's correlations of Cu with other trace

300 elements were performed in each sampling site. Significant ($p<0.05$) positive

301 correlations between Cu and Cs ($r^2 = 0.790$, $p = 0.03$), and between Cu and Tl ($r^2 =$

302 0.790, $p = 0.03$) were found in $PM_{2.5}$ in E1. Copper in $PM_{2.5}$ in E2 exhibited

303 significant positive correlations with Ge, Pb, Tl, V ($r^2 = 0.771$- 0.886), at $p < 0.05$ and

304 W ($r^2 = 0.935$) at $p < 0.01$. Moreover, in $PM_{2.5}$ there were significant positive

305 correlations between Cu and Cd, Ce, Mn, Sn ($r^2 = 0.721$ - 0.851) at $p < 0.05$, while Te

306 ($r^2 = 0.899$) and W ($r^2 = 0.968$) at $p <0.01$ in E4. In TSP, significant positive

307 correlations with Cu was found for Co, Cs and W ($r^2 = 0.714$ - 0.766, $p < 0.05$) in E1,

308 W ($r^2 = 0.954$, $p < 0.01$) in E2, as well as Ni ($r^2 = 0.717$, $p = 0.03$), Te ($r^2 = 0.798$, $p =$

309 0.04) and W ($r^2 = 0.987$, $p < 0.001$) in E4. There were no significant correlations

310 between Cu and other trace elements in E3, neither in $PM_{2.5}$ nor in TSP. Significant

311 positive correlations between Cu and different trace elements were found in different

312 e-waste recycling parks implying different recycled e-waste products, or different

313 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^-, SO_4^{2-}, NH_4^+ and NO_3^-) in $PM_{2.5}$ 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 $PM_{2.5}$, and between E3 and E4 in TSP. However, no significant difference ($p > 0.05$) of EC in $PM_{2.5}$ 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 $PM_{2.5}$ 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 $PM_{2.5}$ from our previous study (Ding et al., 2018), the levels of NH_4^+ in this region were relatively constant (5.14 vs.

3.96 $\mu g/m^3$, in 2013-2014 vs. present, respectively), while those of Cl^- (1.46 vs. 0.32 $\mu g/m^3$) and SO_4^{2-} (13.4 vs. 2.20 $\mu g/m^3$) showed a decreasing trend after introduction of new local policy (Liu, 2015). However, concentrations of NO_3^- in this area were more than twice higher than those found in 2013 by Ding et al. (2018) (4.09 vs. 10.9 $\mu g/m^3$, 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 Chongqing, 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 $PM_{2.5}$, 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 $NH4^+$ in TSP, in e waste parks (8.37 vs. 1.14 $\mu g/m^3$).

Significant correlations between NH_4^+ and NO_3^- ($r^2 = 0.673$, $p < 0.001$) and SO_4^{2-} ($r^2 = 0.386$, $p = 0.002$) were observed, while no significant correlations were found between NH_4^+ and Cl^- in $PM_{2.5}$. A strong correlation between NH_4^+ and NO_3^- means more formation of NH_4NO_3 rather than $(NH_4)_2SO_4$ and NH_4HSO_4 in $PM_{2.5}$. Even more significant correlations between NH_4^+ and NO_3^- ($r^2 = 0.930$, $p < 0.001$), SO_4^{2-} ($r^2 = 0.411$, $p = 0.001$) and Cl^- ($r^2 = 0.290$, $p < 0.008$) were found in TSP. These results suggest that, at present, NH_4NO_3 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 sulphate. The remaining NH_3 may also react with nitric acid to 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 Figure 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 anthropogenic activities to form $PM_{2.5}$. The composition of TSP in E2 presented similar components with $PM_{2.5}$, 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 $PM_{2.5}$ 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 $PM_{2.5}$ and 16.6 - 31.6% in TSP), OM+EC (18.9- 27.8% in $PM_{2.5}$ and 18.7-24.1% in TSP) and SIA (14.1 - 29.1% in $PM_{2.5}$ 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$_{2.5}$, 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 PM2.5 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 PM2.5 (Figure 4). A pair of two-dimension model was created one for TSP and other for PM$_{2.5}$, explaining 67% and 81% of the data variance. In TSP model, first 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 PM2.5 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 PM2.5, 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 ($1.4 \cdot 10^{-2}$ and $1.2 \cdot 10^{-2}$ 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 Figure 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 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 $PM_{2.5}$ in

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the four e-waste sampling sites, and Cr (VI) and Ni in $PM_{2.5}$ 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 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_{10} are considered but in present study,

we estimated the human health risk with $PM_{2.5}$. Therefore, higher risk levels would be

expected if risks were calculated using the levels of trace elements in PM_{10}.

4. Conclusions

TSP and $PM_{2.5}$ 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 $PM_{2.5}$ to individuals living in the neighborhood were also 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. 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 $PM_{2.5}$. 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 indicates a high carcinogenic risk in BG sites.

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Table 1

Levels (mean ±SD) of trace elements in PM$_{2.5}$ and TSP samples collected in 2016 near four e-waste recycling parks (E1, E2, E3 and E4) and a background area (BG)

	PM$_{2.5}$					TSP				
	E1	**E2**	**E3**	**E4**	**BG**	**E1**	**E2**	**E3**	**E4**	**BG**
	(n=5)	**(n=5)**	**(n=5)**	**(n=5)**	**(n=2)**	**(n=5)**	**(n=5)**	**(n=5)**	**(n=5)**	**(n=2)**
Al	915±340	621±645	785±439	841±651	568±337	1267±937	1267±937	665±402	2641±1194	3620±2669
As	13.0±5.33	12.1±6.84	9.26±4.64	7.35±3.67	6.64±1.19	22.6±9.97	16.6±10.2	11.7±3.72	12.3±6.90	22.6±20.3
Ba	264±65.9	ND	ND	ND	235±38.5	ND	ND	ND	ND	977±379
Bi	3.72±1.15	2.79±1.23	3.31±1.07	3.37±2.76	1.34±0.06	3.90±1.38	3.23±1.42	4.28±1.31	3.82±2.74	3.76±1.85
Ca	4229±319	4035±479	3956±485	4282±937	4011±396	5242±844	5708±1354	5420±936	8641±1829	21100±11943
Cd	3.92±1.63	3.23±2.24	3.80±3.63	3.15±2.16	2.66±1.80	4.59±1.64	3.32±2.57	6.85±9.04	3.69±1.79	4.54±0.42
Ce	1.09±0.24	1.27±0.23	0.98±0.22	1.26±0.56	1.14±0.28	1.04±0.72	2.23±1.27	0.93±0.50	2.49±2.43	9.03±6.87
Co	0.42±0.17	0.29±0.14	0.26±0.09	0.27±0.17	0.42±0.09	0.95±0.59	0.62±0.44	0.67±0.35	1.06±0.63	2.87±2.54
Cr	34.7±4.21	ND	ND	ND	39.1±9.61	53.8±11.2	ND	ND	ND	180±81.4
Cs	0.46±0.13	0.25±0.14	0.26±0.14	0.37±0.19	0.54±0.003	0.39±0.15	0.52±0.33	0.33±0.15	0.57±0.31	0.60±0.20
Cu	221±127	242±143	83.5±17.1	102±93.0	32.4±1.77	373±202	894±581	134±16.0	368±305	284±229
Dy	0.19±0.03	0.17±0.05	0.22±0.06	0.22±0.09	0.14±0.02	ND	ND	ND	ND	0.25±0.04
Er	0.09±0.02	0.06±0.04	0.09±0.03	0.09±0.05	ND	ND	ND	ND	ND	0.09±0.02
Eu	0.07±0.01	ND	ND	ND	0.10±0.02	ND	ND	ND	ND	0.39±0.15
Fe	377±71.5	422±134	337±102	342±103	471±202	1126±332	1369±453	1111±320	1564±546	4025±3518
Gd	0.17±0.02	0.16±0.02	0.17±0.04	0.18±0.06	0.12±0.01	ND	ND	ND	ND	0.48±0.07
Ge	1.31±0.46	1.12±0.50	1.22±0.37	1.30±0.71	1.38±0.12	ND	ND	ND	ND	5.80±3.23
Hg	ND	ND	ND	ND	ND	ND	0.20±0.12	ND	ND	ND
K	1375±268	1101±372	643±333	939±501	1187±107	1506±408	1017±521	ND	772±556	6137±3701
La	0.52±0.10	0.56±0.13	0.47±0.15	0.49±0.14	0.53±0.12	0.22±0.20	0.63±0.44	0.35±0.23	0.79±0.78	3.22±2.23

Li	1.47±0.51	1.31±0.42	1.12±0.34	1.51±0.64	1.20±0.43	0.45±0.53	0.97±0.94	0.46±0.37	1.30±1.48	4.01±3.41
Mg	252±332	497±425	745±332	877±631	ND	ND	ND	ND	ND	ND
Mn	20.4±5.99	25.6±7.97	18.3±5.14	23.2±10.5	29.6±9.03	40.9±14.1	53.0±16.3	40.3±11.3	61.9±22.4	133±107
Mo	38.9±7.78	56.0±6.19	54.4±7.36	57.1±15.4	41.5±7.89	ND	ND	ND	ND	181±79.3
Na	10500±960	11244±405	10460±1008	11714±2503	9592±2587	11261±1070	14676±1430	12716±1522	14389±4291	43896±19279
Nd	0.44±0.06	0.49±0.10	0.49±0.10	0.40±0.08	0.42±0.03	0.12±0.11	0.56±0.41	0.39±0.30	0.62±0.59	2.58±1.53
Ni	91.7±11.0	10.2±2.12	10.0±1.61	12.2±2.20	78.8±21.3	193±12.0	12.5±4.42	11.5±2.38	16.6±3.50	380±144
Pb	121±64.9	91.6±60.6	85.6±23.6	78.2±40.2	30.1±5.03	145±75.6	113±79.2	126±34.0	183±131	89.5±76.4
Pr	0.12±0.01	0.13±0.03	0.12±0.03	0.10±0.02	0.11±0.11	0.05±0.03	0.18±0.11	0.11±0.06	0.19±0.17	0.71±0.41
Rb	3.80±0.95	2.64±1.90	2.16±1.29	3.22±1.63	3.66±0.38	3.74±1.29	4.20±3.54	1.27±1.61	4.96±4.24	10.2±6.94
Sb	16.4±14.0	6.24±4.55	7.43±2.68	9.48±8.15	3.34±1.63	17.0±21.0	3.68±4.70	4.50±3.02	8.32±10.7	9.65±10.6
Sc	ND	ND	ND	ND	ND	ND	ND	ND	ND	12.5±15.2
Sm	0.10±0.01	0.11±0.01	0.11±0.03	0.09±0.02	0.08±0.01	ND	ND	ND	0.04±0.02	0.41±0.22
Sn	65.7±42.7	28.7±29.4	7.19±2.49	16.2±12.7	8.75±0.48	84.8±41.6	35.2±35.3	10.4±3.26	21.9±16.1	22.6±15.8
Sr	7.43±1.58	ND	ND	ND	7.58±0.32	ND	ND	ND	ND	42.9±27.8
Te	ND	1.15±0.13	1.22±0.10	1.17±0.18	ND	1.19±0.32	4.29±0.32	4.36±0.11	4.51±0.60	ND
Ti	34.8±7.66	40.5±10.0	27.1±7.87	32.2±15.0	48.1±12.9	97.7±34.1	131±50.8	74.2±21.6	176±115	413±318
Tl	0.51±0.25	0.49±0.30	0.58±0.15	0.56±0.32	0.51±0.27	0.42±0.29	0.53±0.36	0.74±0.20	0.76±0.29	0.53±004
U	0.34±0.08	0.36±0.05	0.35±0.07	0.36±0.12	0.28±0.05	ND	ND	ND	ND	1.44±0.90
V	5.84±3.08	5.59±4.44	ND	9.42±4.91	4.13±3.35	5.31±3.37	5.87±5.65	ND	12.4±6.75	16.6±16.8
W	0.72±0.46	6.32±3.30	2.45±0.66	1.91±1.91	1.49±0.27	0.93±0.69	30.7±20.5	3.51±0.83	7.27±6.70	13.4±11.8
Y	1.12±0.31	0.56±0.41	0.85±0.37	0.99±0.74	0.71±0.20	ND	ND	ND	0.17±0.27	0.57±0.30
Yb	0.10±0.02	0.05±0.03	0.06±0.04	0.08±0.05	0.05±0.03	ND	ND	ND	ND	0.12±0.04
Zr	5.86±1.84	9.08±0.95	8.06±1.71	8.13±3.17	7.10±0.47	ND	ND	ND	ND	42.4±21.3

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

Table 2

Levels of organic carbon (OC), elemental carbon (EC), ions (Cl$^-$, SO$_4^{2-}$, NH$_4^+$ and NO$_3^-$) and indirect determinations (OM, CO$_3^{2-}$, SiO$_2$ and Al$_2$O$_3$) in PM$_{2.5}$ and TSP samples collected near four e-waste recycling parks (E1, E2, E3, E4) and a background area (BG) in 2016.

	PM$_{2.5}$					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±1.68	10.9±3.57	5.76±1.20	9.18±4.56	5.13±0.73	12.0±1.63	15.1±3.90	9.21±1.37	15.6±5.89	14.2±1.22
EC	2.81±0.45	3.08±1.03	1.85±0.18	3.17±1.86	2.54±0.52	3.68±1.02	3.80±1.77	2.25±0.25	4.63±3.07	4.56±0.71
OC+EC	11.1±1.92	14.0±4.49	7.62±1.16	12.4±6.32	7.67±1.25	15.6±2.48	18.9±5.53	11.5±1.53	20.2±8.64	18.7±1.93
OM	13.3±2.69	17.5±5.71	9.22±1.93	14.7±7.29	8.21±1.16	19.1±2.61	24.2±6.24	14.7±2.19	24.9±9.43	22.6±1.95
CO$_3^{2-}$	6.97±0.73	7.29±1.22	7.80±1.19	8.62±2.83	6.02±0.59	7.94±1.27	8.64±2.03	8.20±1.40	13.0±2.74	31.7±17.9
SiO$_2$	5.19±1.93	3.52±3.65	4.45±2.49	4.77±3.69	3.21±1.91	8.73±2.43	7.18±5.31	3.77±2.28	15.0±6.77	20.5±15.1
Al$_2$O$_3$	1.73±0.64	1.17±1.21	1.43±0.83	1.59±1.23	1.07±0.64	2.91±0.81	2.39±1.77	1.26±0.76	4.99±2.26	6.84±5.05
Cl$^-$	0.34±0.27	0.26±0.07	0.20±0.01	0.50±0.46	0.13±0.15	0.27±0.21	0.53±0.08	0.43±0.02	0.73±0.30	0.69±0.38
SO$_4^{2-}$	1.02±0.39	3.05±3.07	0.79±0.03	3.96±3.89	0.59±0.53	0.95±0.46	2.89±1.62	1.80±0.13	5.32±3.80	2.27±2.23
NH$_4^+$	1.86±0.70	5.85±2.69	4.04±1.18	4.10±2.69	1.25±0.51	3.47±1.35	11.4±4.85	9.15±2.71	9.45±4.97	1.14±0.76
NO$_3^-$	4.95±2.12	15.2±5.59	12.5±3.79	11.0±6.18	4.54±0.92	6.67±1.94	16.3±6.79	13.1±3.52	14.0±4.38	10.2±9.56

Levels in μg/m^3. OC+EC: organic carbon plus elemental carbon. OM: organic matter.

Table 3

Outdoor and indoor (modeled with IAQX software) PM$_{2.5}$ concentrations and exposure levels in e-waste recycling sites (E1 to E4) and a background area (BG).

	Concentration (µg/m^3)		Exposure (mg/(kg·day))			
	Outdoor	**Indoor**	**Sleeping**	**Work/Leisure**	**Outdoor**	**Sum**
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

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	Be	Cd	Co	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).
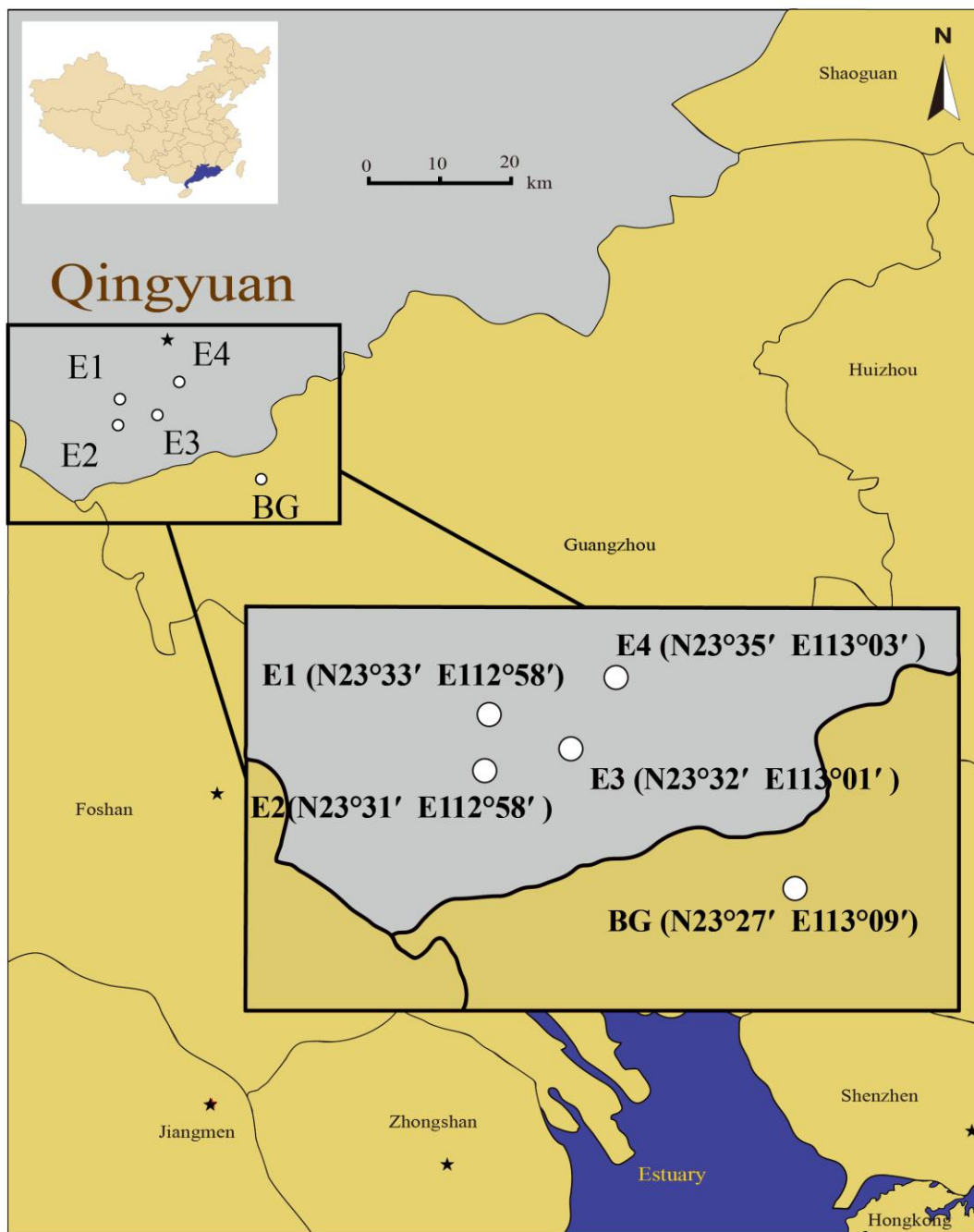
Figure 1: Sampling sites near e-waste recycling parks (E1, E2, E3 and E4) and a background (BG) location.
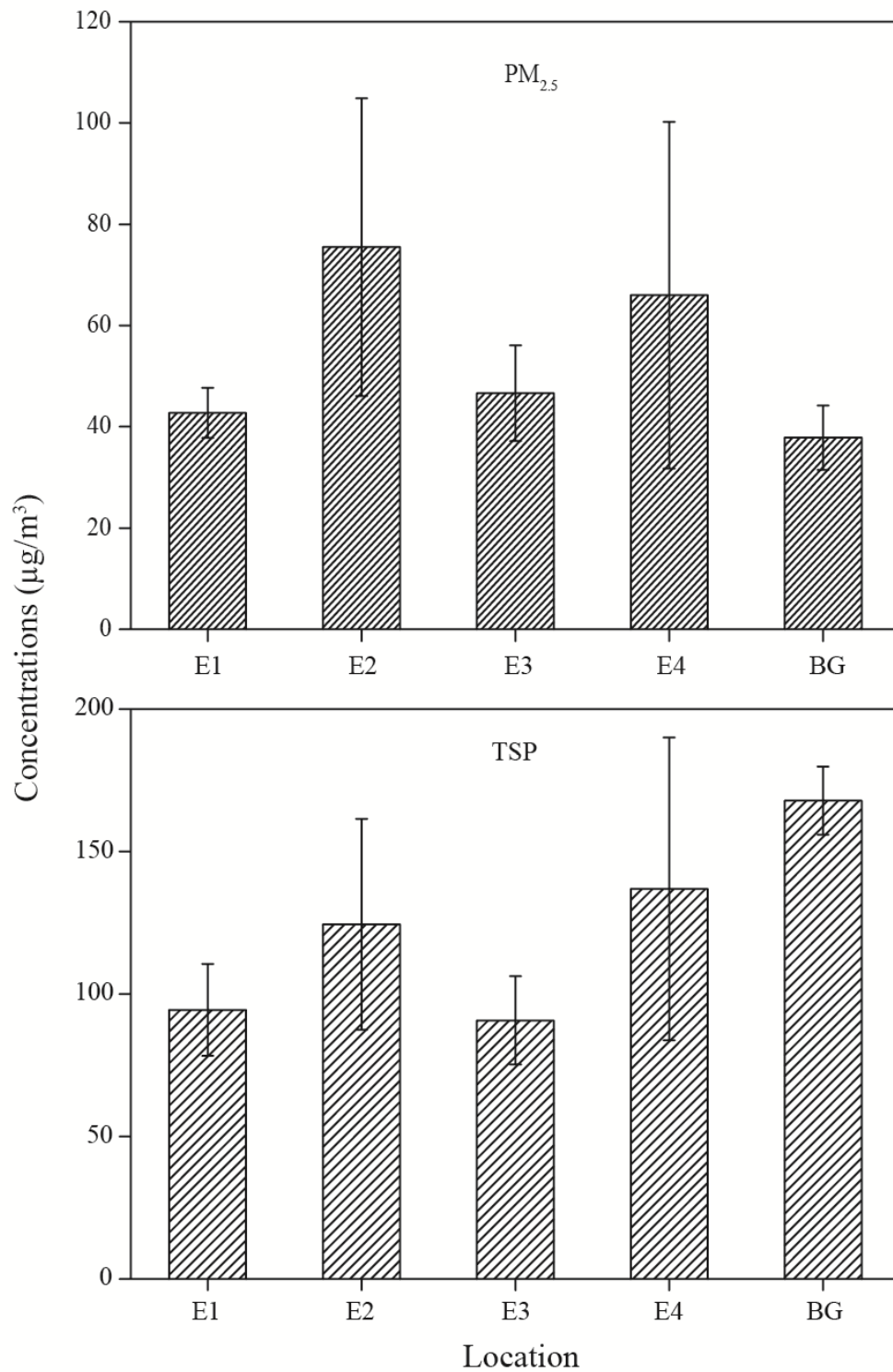
Figure 2: Total suspended particles (TSP) and PM$_{2.5}$ levels (average + standard deviation) in the four sampling sites around e-waste recycling parks (E1, E2, E3 and E4) and in a background (BG) location.
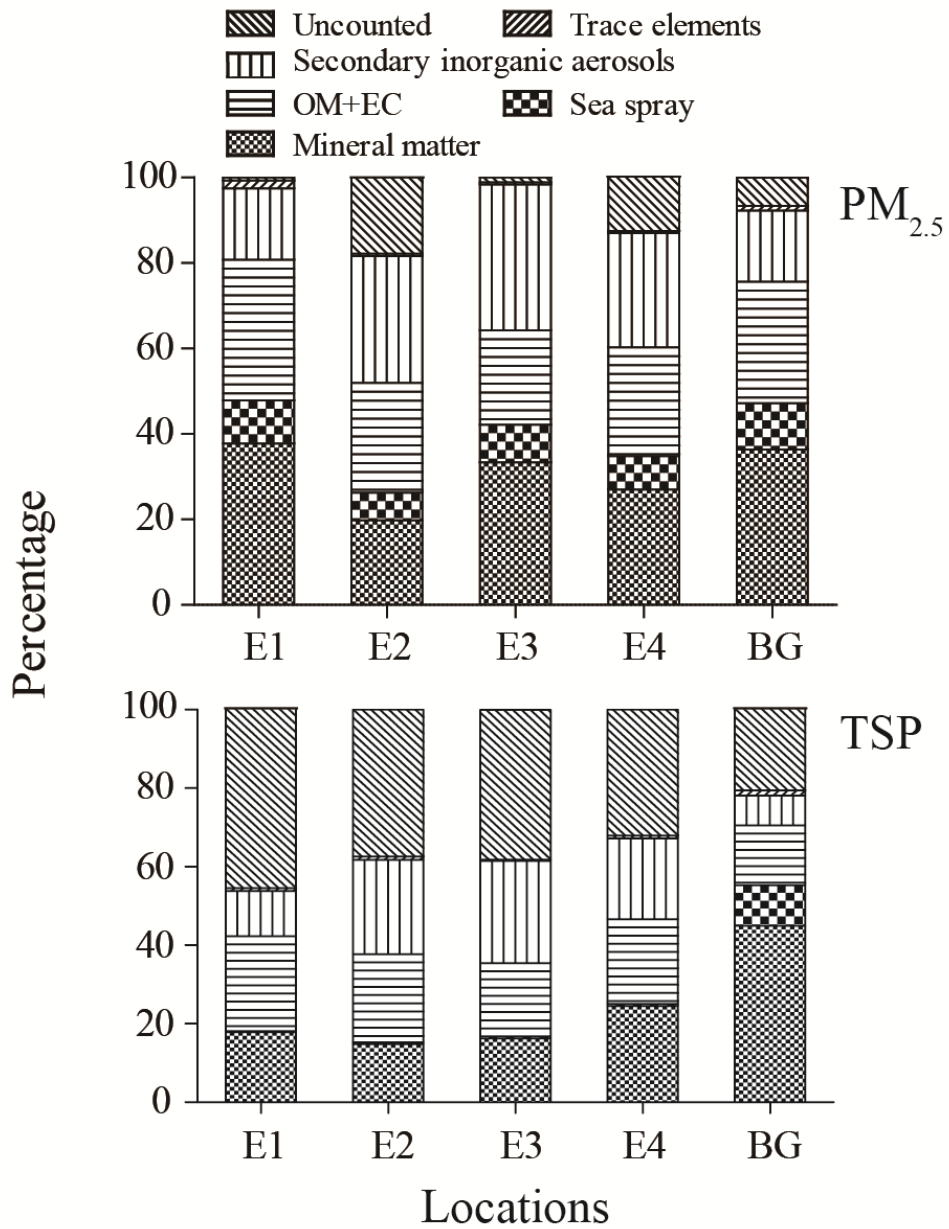
Figure 3: Main components of collected $PM_{2.5}$ and TSP around the four e-waste recycling sites and a background area. Results are expressed as percentage of the mass.
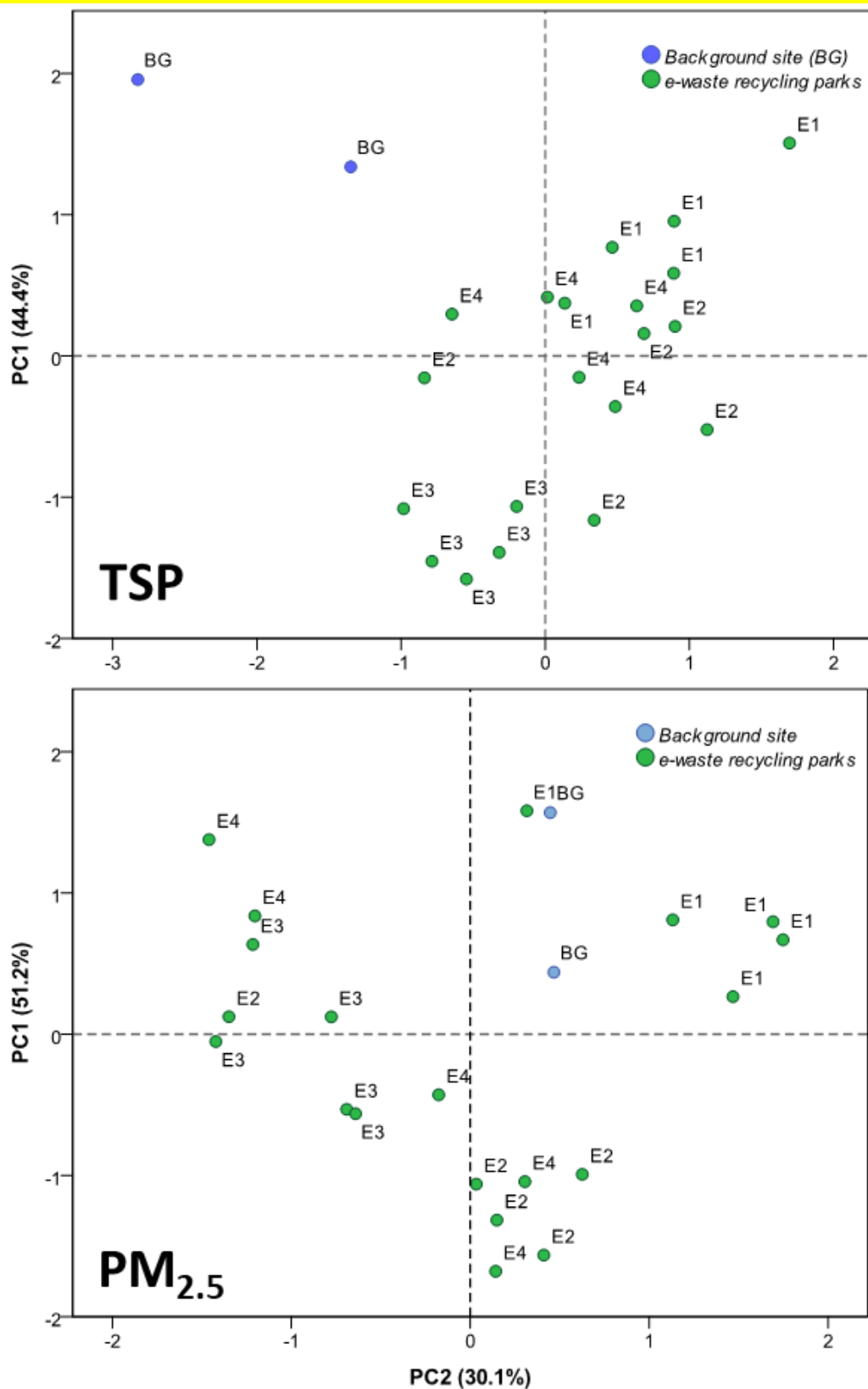
Figure 4: Principal component analysis of main components of TPS and PM$_{2.5}$ collected in four e-waste recycling parks (from E1 to E4) and background site (BG).
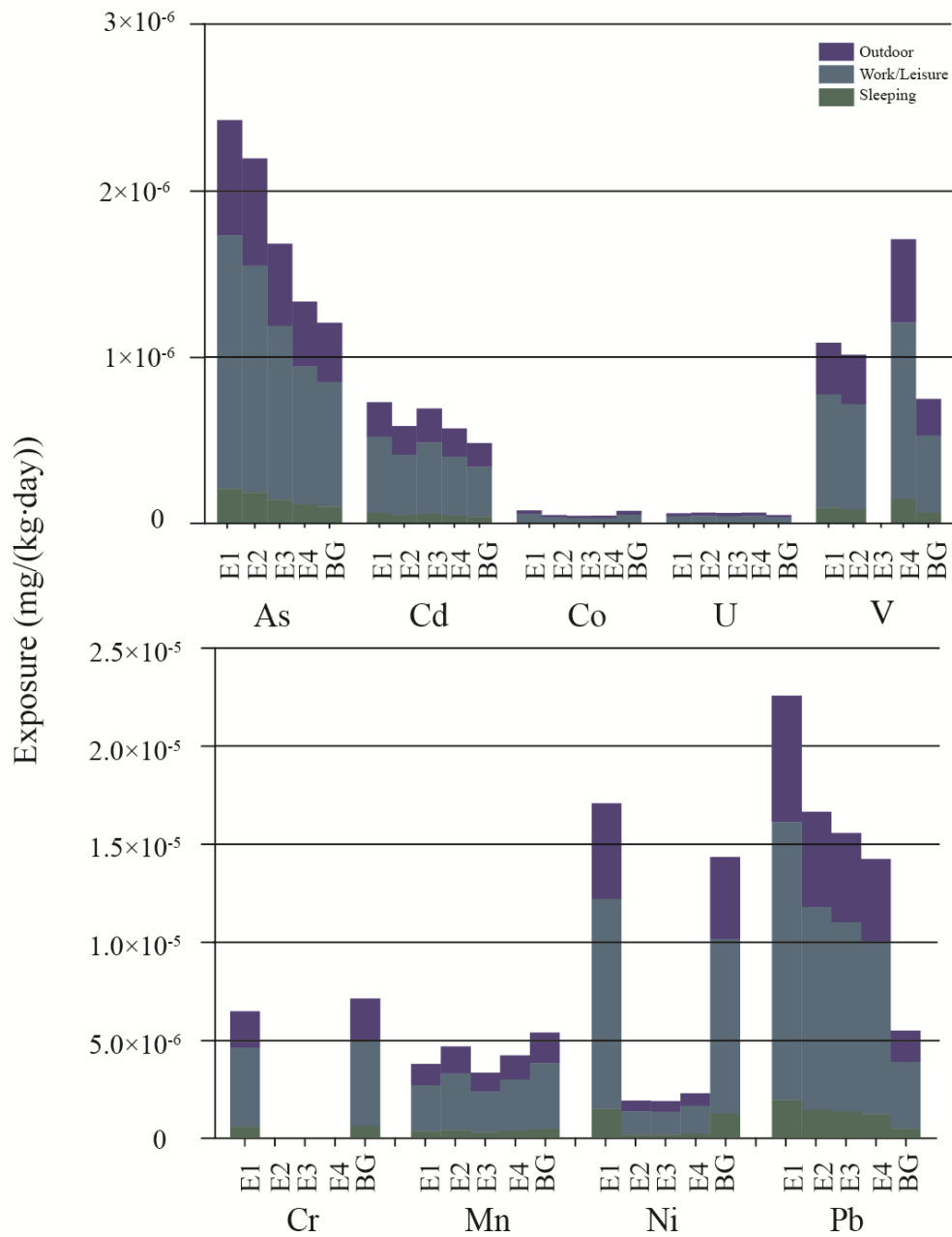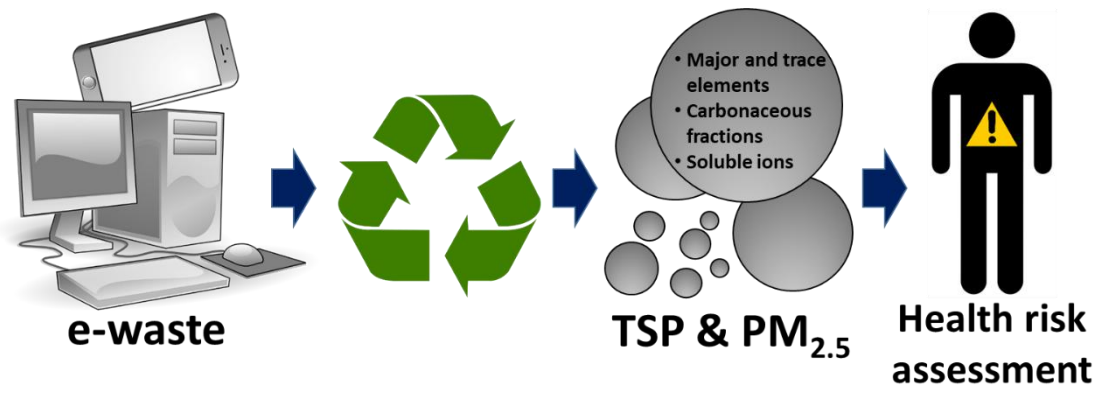
Figure 5: Inhalation exposure to toxic elements contained in PM$_{2.5}$ from e-waste recycling parks (E1 to E4) and a background area (BG).

e-waste

• Major and trace
  elements
• Carbonaceous
  fractions
• Soluble ions

TSP & PM$_{2.5}$

Health risk
assessment

*Highlights (for review : 3 to 5 bullet points (maximum 85 characters including spaces per bullet point)

Highlights

- TSP and PM$_{2.5}$ composition around e-waste recycling region were determined
- Levels of TSP and PM$_{2.5}$ were lower with advanced recycling methods
- High positive correlations between Cu and both W and Te levels were found
- High carcinogenic risks were found