E-waste driven pollution in Pakistan: The first evidence of environmental and human exposure to flame retardants (FRs) in Karachi City

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1   **Abstract**

2   Informal e-waste recycling activities have been shown to be a major emitter of organic flame

3   retardants (FRs), contributing to both environmental and human exposure to laborers at e-waste

4   recycling sites in some West African countries, as well as in China and India. The main objective

of this study was to determine the levels of selected organic FRs in both air and soil samples collected from areas with intensive informal e-waste recycling activities in Karachi, Pakistan. Dechlorane Plus (DP) and "novel" brominated flame retardants (NBFRs) were often detected in high concentrations in soils, while phosphorous-based FRs (OPFRs) dominated atmospheric samples. Among individual substances and substance groups, decabromodiphenyl ether (BDE-209) (726 ng/g), decabromodiphenyl ethane (DBDPE) (551 ng/g), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE) (362 ng/g) and tri-phenyl-phosphate ($\sum$TPP) (296 ng/g) were found to be prevalent in soils, while OPFR congeners (5903-24986 ng/m^3) were prevalent in air. The two major e-waste recycling areas (Shershah and Lyari) were highly contaminated with FRs, suggesting informal e-waste recycling activities as a major emission source of FRs in the environment in Karachi City. However, the hazards associated with exposure to PM$_{2.5}$ appear to exceed those attributed to exposure to selected FRs via inhalation and soil ingestion.

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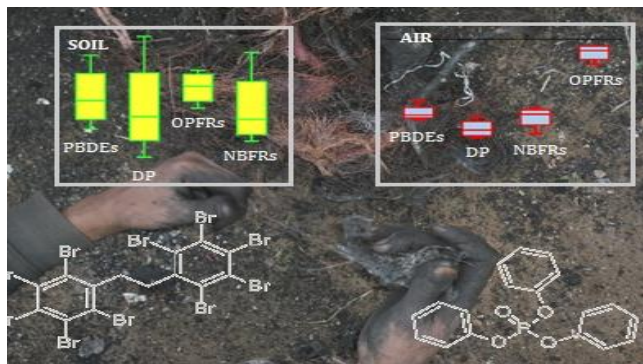
1. Introduction

With the increasing use of electronics and electrical equipment (EEE) and their decreasing life spans, significant quantities of EEE are becoming obsolete and discarded across the world[1]. Electronic and electrical waste (e-waste) is a heterogeneous mixture of plastics, glass, metals and ceramics, as well as toxic chemicals, such as organic flame retardants (FRs), polychlorinated

24   biphenyls (PCBs), metals and various other potentially hazardous compounds[2]. E-waste,

25   therefore, needs to be discarded properly to minimize emissions of hazardous compounds

26   potentially causing adverse effects to environmental and human health. Developing countries are

27   considered particularly vulnerable because recycling is often carried out informally and because

28   additional e-waste is typically imported from developed countries[3-4].

29   Pakistan has been identified as one of the major importers of e-waste among developing

30   countries, which adds to the generation of an estimated 317 kt of domestic e-waste in 2015[5].

31   Karachi is one of the most urbanized, industrialized and populated coastal cities in the world.

32   This city hosts two major sea ports, and there are extensive industrial activities within and

33   around the city. Karachi receives tons of imported, old and obsolete EEE from all around the

34   world, which, in turn, is traded from vendors to scrap dealers and dismantlers who recycle the e-

35   waste, at the possible expense of their health, to extract valuable materials from the waste. The

36   informal practices used for the recycling of e-waste in Karachi mainly involve open air burning,

37   dismantling or shredding, acid baths and melting. The remaining waste, which cannot be

38   recycled or reused, is often dumped in landfills or surrounding water bodies.

39   Recently, international attention has been drawn towards possibly adverse effects of organic

40   flame retardants (FRs), which are released from e-waste recycling, on human and environmental

41   health[6-7]. Different FRs are incorporated into different polymeric substances to meet various fire

42   safety standards[8]. These FRs are typically used in cable insulation, plastic housings, and circuit

43   boards of EEE[9]. However, international regulations, such as the Stockholm Convention (SC) on

44   persistent organic pollutants (POPs), have led to a shift in the production and use of various FRs,

45   thereby affecting the chemical content of FRs in e-waste. For example, octa-BDE, penta-BDE

46   and deca-BDE mixtures are now regulated under the SC, which collectively led to a reduction in

47 the use of polybrominated diphenyl ethers (PBDEs), potentially at the expense of novel

48 brominated flame retardants (NBFRs), organophosphate flame retardants (OPFRs) and

49 Dechlorane Plus (DP)[10]. Residents and workers involved in informal e-waste recycling could be

50 exposed to these FRs through inhalation, ingestion (e.g., soil and food contamination) or dermal

51 contact[11]. Health risks are hypothesized to be higher for workers than residents because workers

52 are directly exposed to e-waste and various FR chemicals.

53 While there have been some studies related to e-waste in Pakistan[5], including informal e-waste

54 recycling[12-13], there is limited information on possible environmental and human exposure to FRs

55 from e-waste recycling activities. This study is the first to present measurements of selected FRs

56 in soil and air from the largest e-waste recycling sites in Pakistan and to include an initial

57 exposure assessment (air inhalation and soil ingestion) of laborers in the study area.

58 **2. Materials and methods**

59 **2.1. Sampling**

60 Four e-waste recycling sites were identified in Karachi City for soil and air sampling (Table S1).

61 These sites were Jacob Lines (JC), Surjani Town (SJ), Lyari (LY) and Shershah (SS) (S1). A

62 total of 21 surface soil (0-10 cm) samples were collected from these e-waste recycling sites. A

63 map of Karachi, including the soil sampling locations, is shown in Figure S1. Soil samples were

64 collected within a 500-m distance from these four e-waste sites. Each soil sample was collected

65 using a soil auger. The samples were then freeze-dried and manually homogenized after the

66 removal of pebbles, weeds, and twigs. Sieved samples (<2.0 mm) were collected and stored in

67 amber glass bottles at −20°C prior to chemical analysis.

68 A total of four active air samples were collected in this study. These samples were collected in

69 the immediate vicinity of each e-waste recycling site (Figure S1) using a high volume active air

70 sampler (Guangzhou Mingye Huanbao Technology Company), which was equipped with a $PM_{2.5}$

71 inlet. Each sample was collected on the rooftops of two-story buildings (~10 m height) for a

72 continuous 24-h period at a flow rate of ~18 m^3/h during the period August 16-26, 2014.

73 Gaseous and particulate phases were collected on Polyurethane Foam (PUFs) (pre-extracted with

74 acetone and hexane for 48-h each) and prebaked (450°C, 6 h, muffle furnace) quartz fiber filters

75 (20×25 cm^2, 2600 QAT, PALL, USA), respectively, and then analyzed separately. Field blanks

76 (3 PUFs and 3 filters) were assembled in an active sampler at the sampling sites and then

77 disassembled after approximately 5 minutes. After the filters and PUFs were collected, the

78 samples were wrapped in aluminum foil and stored in Ziploc© bags at -20°C until further

79 analysis. Details of the sampling sites are presented in the Supporting Information (section S1).

80 Meteorological conditions during the sampling campaign are given in Figure S2. Mass

81 concentrations of $PM_{2.5}$ were determined gravimetrically, and further details are included in the

82 Supporting Information (section S2).

83 **2.2. Analysis of FRs**

84 The treatment, analytical procedures and instrumental analysis used to determine FRs in soil and

85 atmospheric samples are described in the SI (section S3).

86 **2.3. QA/QC**

87 To assess potential sample contamination and the repeatability of the analysis, a procedural

88 blank, a spiked blank containing all the chemicals investigated, and a duplicated sample were run

89 with each batch of samples (10 per batch). Method detection limits (MDLs) were calculated

90 according to the US EPA method 5055 (Table S2). The MDLs were defined as the average

91 values of the field blanks plus 3 times the standard deviation of the field blank values. When

92 compounds were not found in the field blanks, the MDLs were calculated as 3 times the

93 instrumental detection limits (IDLs). The IDLs were calculated from the lowest standards and

94 extrapolated to the corresponding amount of analyte that would generate a signal-to-noise ratio

95 of 3:1.

96 Except for BDE-209 (mean = 0.089 ng), TBP (mean = 0.912 ng) and TDCPP (mean = 0.071 ng),

97 none of the other compounds were detected in the procedural and laboratory blanks. The

98 surrogate recoveries for PCB-30, PCB-198, PCB-209 and TCEP-d12 in all samples were

99 $67\pm14\%$, $72\pm10\%$, $79\pm19\%$ and $86\pm9\%$, respectively. The results were corrected based on

100 surrogate recovery rates and blank values.

101 **2.4. Statistical analysis**

102 Descriptive statistics were calculated using Microsoft Excel (2010), XLstat (2015.2) and SPSS

103 21 (IBM). Correlations between components were presented as Pearson's correlations. Graphical

104 presentation through bar graphs and box plots were made using SPSS (IBM). Spatial distribution

105 maps for contaminant levels in the study area were generated with ArcGIS version 9.3 using

106 satellite images obtained from Google Inc.

107 **2.5. Human health exposure**

108 The present study also aimed to estimate selected exposure pathways for laborers working at e-

109 waste recycling sites in Karachi. The study assumes that laborers at e-waste sites are exposed to

110 accidental soil ingestion and inhalation while burning and treating the e-waste. This is only a

111 "partial" estimate, which may be under biased in terms of total exposure, as it does not consider

112 other exposure pathways of potential significance (e.g., dermal exposures and diet from local

113 produce). Second, since air samples were collected on the rooftops of buildings, they may not

114 accurately represent the inhalation experienced by the workers. For inhalation (air) and ingestion

115 (soil), average daily doses (ADDx) and average lifetime doses (LADDx) were calculated.

116   Inhalation (Eqs. 1 and 2) and ingestion (Eqs. 3 and 4) were calculated according to the following

117   equations provided by US EPA exposure assessment tools[14];

118     $$\textbf{LADDair = Cair x InhR x ET x EF x ED / BW x LT} \qquad \textbf{(1)}$$

119     $$\textbf{ADDair = CairxInhR x ET x EF x ED/BW x AT} \qquad \textbf{(2)}$$

120     $$\textbf{ADDsoil = Csoil x IngR x EF x ED / BW x AT} \qquad \textbf{(3)}$$

121     $$\textbf{LADDsoil = Csoil x IngR x EF x ED / BW x LT} \qquad \textbf{(4)}$$

122   Factors needed for the calculations were obtained from similar studies and US EPA

123   recommended settings. Details are given in Tables S3 and S4.

124   **3. Results and discussion**

125   **3.1. Average 24-h concentration of PM$_{2.5}$**

126   The average 24-hour concentrations of PM$_{2.5}$ collected from e-waste sites in Karachi are

127   displayed in Figure S3. The overall 24-h average concentration of PM$_{2.5}$ was highest at SS, with

128   a value of 964 µg/m^3, followed by LY (823 µg/m^3), SJ (128 µg/m^3) and JC (74.4 µg/m^3). The

129   levels were considerably higher than WHO ambient air standards (25 µg/m^3)[15] and, to the best of

130   our knowledge, were the highest reported among published data from e-waste sites (e.g., Guiyu

131   (62 µg/m^3), Hong Kong (32–55 µg/m^3) and Guangzhou (105-112 µg/m^3))[16]. Another study from

132   e-waste sites in Guiyu reported comparably low levels of PM$_{2.5}$ (50 µg/m^3)[17]. Our findings are,

133   however, in line with some studies reporting elevated concentrations from different cities in

134   Pakistan. Lahore is the most studied city with respect to mass concentrations of particulate

135   matter (PM), where reported average values of PM$_{2.5}$ range between 36.0-209 μg/m^3 at urban

136   and rural sites [18-21]. Studies of Islamabad reported average PM$_{2.5}$ readings of 8.10 μg/m^3 [22], 7.80

137   μg/m^3 [23], and 8.20 μg/m^3 [23]; studies of Karachi, 83.5 μg/m^3 [24].

3.2.   Occurrence and distribution pattern

While FRs have been studied in indoor environmental matrices in Pakistan [25-26], this is the first study on FRs from e-waste recycling sites. Eight PBDEs, six NBFRs, seven OPFRs congeners and two DP compounds were identified and quantified in both surface soils and ambient air from e-waste recycling sites in Karachi. The overall results and basic descriptive statistics of concentrations of FRs in both soil and air are summarized in Tables S5 and S6. Measured concentrations for all FRs were highest around the largest e-waste recycling area (SS), where BDE-209, BDE-153, BDE-154, DBDPE, BTBPE and DP and its isomers (*syn*-DP and *anti*-DP) were detected in concentrations up to mg/g in soil. As the FR concentrations were much higher at SS compared to LY, SJ and JC, standard deviations were very high for the whole dataset, which indicated substantial inter-site variation in concentrations.

3.2.1.   Soil

All target analytes detected in surface soil samples were collected from four e-waste recycling sites. The concentrations of ∑PBDEs, ∑OPFRs, ∑NBFRs and ∑DP in soil ranged from 0.40-12754 ng/g, 46.6-1689 ng/g, 0.30-8110 ng/g and ND-26239 ng/g, respectively. Table S7 shows the correlation among FRs in soil. Most of the FRs have positive and significant correlations, indicating one or more common emission source for these FRs.

∑PBDEs: Among PBDE congeners (Table S6), BDE-209, BDE-183 and BDE-153 were most prevalent in soil samples with average values of 726 ng/g, 47 ng/g, and 46 ng/g across all sites, respectively. ∑PBDE levels in SS were 2 orders of magnitude higher than at other sites (Figure 1). BDE-209 was highest in SS, with a mean concentration of 2994 ng/g, ranging from 0.50-11881 ng/g, while BDE-183 was most prevalent at LY, with a mean of 169 ng/g. The results indicate that the commercial deca-BDE, octa-BDE and penta-BDE mixtures were major

contaminants, as also reported in various studies from China[27-28]. The concentrations of ∑PBDEs were consistent with those reported in studies from China[29-30] but were lower than soil concentrations from burning, dumping and e-waste recycling workshops in China and Vietnam[31-33]. However, levels in the present study were higher than those in past studies from urban/agricultural areas in Pakistan (0.036 ng/g [34], 0.0033 ng/g [35] and 0.011 ng/g [36]. Overall, the levels of ∑PBDEs were lower than levels found in studies that were conducted at e-waste recycling sites in Guiyu[27], which is considered one of the major informal e-waste recycling areas of the world. BDE-209 contributed 83% of the ∑PBDEs detected in soil samples, which is not surprising since deca-BDE is the most extensively used commercial product of PBDE, following initial bans on penta- and octa-BDE[37]. The concentrations of BDE-209 were very similar to those found in previous reports studying e-waste sites and urban sites[8, 27, 34, 38], which suggests that e-waste containing technical deca-BDE are processed within Karachi.

∑DP: The average concentration of ∑DP (3398 ng/g) in all soil samples was very high but comparable to an e-waste recycling site in Guiyu where ∑DP levels were 3327 ng/g [39]. This value is higher than that in the samples collected in the vicinity of a DP manufacturing facility in Huai'an City, China, which had concentrations of 1490 ng/g (average) [40], 0.83-1200 ng/g[41] and 35.6 ng/g (average)[42]. Interestingly, soil concentrations were higher than in the vicinity of DP manufacturing facilities, indicating that major emissions from informal e-waste recycling sites may potentially exceed those from production sites[39]. ∑DP levels in all combined soils were also higher in this study than those detected in the urban environments of Pakistan[34-36]. This finding serves to illustrate that sound chemical management strategies need to consider emissions from FRs across the entire life-cycle. Data on soil DP are still limited to a few studies in China[39, 43]. DP is a highly chlorinated compound that is incorporated as an FR in the coating of electrical

184   wires and cables, connectors used in computers and televisions, and plastic roofing [40, 44-45]. We

185   therefore believe the higher concentrations of ∑DP seen in this study are largely dictated by

186   informal e-waste recycling activities in Karachi, including open-air burning, acid stripping,

187   manual dismantling and shredding. The levels of *syn*-DP ranged between ND-10697 ng/g, while

188   *anti*-DP ranged between ND-21620 ng/g. Overall, the levels of *anti*-DP were higher than the

189   levels of *syn*-DP in soils from SS and LY. In contrast, SJ displayed high levels of *syn*-DP, while

190   JC had equal levels of both isomers (Figure 1).

191   *∑OPFRs:* In this study, the high levels of ∑OPFRs in soils were determined to have an average

192   concentration of 458 ng/g across all sites. ∑TPP (296 ng/g), TCEP (93.4 ng/g) and ∑TCPP (55.9

193   ng/g) were dominant in the soil samples, while other ∑OPFRs were detected at lower

194   concentrations. ∑OPFRs were dominant in the following order: SS>LY>JC>SJ (Figure 1). A

195   similar study at e-waste recycling workshops in Vietnam reported average concentrations of 24.0

196   ng/g (EHDPP) and 4.30 ng/g (TCEP), while open burning site levels were 69.0 ng/g (EHDPP)

197   and 2.10 ng/g (TCEP)[8]. Levels reported in samples from a university campus in Germany were

198   low in comparison to our results, with concentrations of TCEP and TCPP ranging from below

199   LOQ (0.60) to 18.2 ng/g and from 0.59 to 8.33 ng/g, respectively[46]. Another study analyzing

200   grasslands in Germany reported average concentrations for TCEP, TCPP, and TPP at 4.96 ng/g,

201   1.23 ng/g and 3.61 ng/g, respectively[47]. TCEP, TPP and TCPP are commonly incorporated as

202   additive FRs in electronics as well as in textiles. TCEP is no longer produced in the EU, though

203   its production and use in the US is still legal and unrestricted [48]. TCEP, TPP and TCPP are

204   physically bound with a polymer matrix of electronics. Hence, recycling operations such as high

205   temperature burning and shredding could cause the release of OPFRs[49]. Other studies have

206   shown that TPP is related to the recycling of printed circuit boards[50-51]. High concentrations of

207   ∑TPP in the study area could be indicative of extensive recycling of waste printed circuit

208   boards[51]. Although levels of ∑OPFRs in soil are below the ∑PBDEs, their presence indicates a

209   possible transition to alternative FRs. For example, a Japanese report on consumer products

210   suggests a predominant use of OPFRs, apart from PBDEs, in electric housings and printed circuit

211   boards[9].

212   *∑NBFRs:* Among ∑NBFRs, DBDPE and BTBPE were the prominent congeners, ranging from

213   0.13-6585 ng/g and 0.09-4150 ng/g, respectively, for all soils combined. As displayed in Figure

214   1, SS was the most contaminated, with an average ∑NBFR concentration of 4241 ng/g, followed

215   by LY (49.6 ng/g), SJ (12.8 ng/g) and JC (4.00 ng/g). DBDPE accounted for 44% to 69% of all

216   NBFRs from all four sites. This finding is not surprising, as DBDPE is one of the alternatives to

217   deca-BDE and was a major FR used worldwide after the ban of deca-BDE under the SC[52-53].

218   DBDPE was higher than all other non-BDE FRs but still lower than BDE-209 for all soils

219   combined. Average concentrations of DBDPE (579 ng/g) in this study were considerably higher

220   than those in studies that analyzed Chinese forest soils (2.64 ng/g)[54], an e-waste site in

221   Guangzhou, China (1.14 ng/g)[55] and areas near e-waste recycling workshops in Bui Dau,

222   Vietnam (39.0 ng/g)[33]. BTBPE exhibited the second highest concentration at all four sites, with

223   an average concentration of 363 ng/g. Soils from the e-waste area in Qingyuan City, China, had

224   an average concentration of 1.98 ng/g, while levels from farmland soil from the same study had a

225   very low mean level of 0.05 ng/g[55]. Outdoor dust samples collected at the surface near e-waste

226   workshops had high levels (107 ng/g) compared to soil samples from the same study, suggesting

227   that these workshops are emitters of BTBPE[55]. Levels of BTBPE in soils around e-waste

228   recycling sites in Bui Dau ranged between 0.51 and 350 ng/g, with a median value of 12.0

229   ng/g[33]. High levels of BTBPE in the present study suggest its use in old and obsolete EEE, as a

230 possible replacement of octa-BDE, which is no longer in production[56]. The concentrations of

231 DBDPE and BTBPE in soil were higher than those values reported in the past. PBEB, HBB and

232 TBB, with average concentrations of 19.0 ng/g, 23.0 ng/g and 10.6 ng/g, respectively, were low

233 in comparison with DBDPE and BTBPE. There is no previous study of NBFRs in soils from

234 Pakistan. However, there are several studies about indoor dust, serum, hair and pet animals in

235 various urban environments[25-26, 57-58]. Taken together, the high concentrations of NBFRs in the

236 present study support the transition of PBDEs to NBFRs.

237 **3.2.2. Air**

238 Levels of $\sum$PBDEs, $\sum$OPFRs, $\sum$NBFRs and $\sum$DP in air samples (particulate+gaseous) ranged

239 between 40.0 and 275 ng/m^3, 5903 and 24986 ng/m^3, 21.0 and 170 ng/m^3 and 15.0 and 85.0

240 ng/m^3, respectively. Table S8 displays correlations among FRs in atmospheric samples. Positive

241 correlations among OPFRs, NBFRs, PBDEs and DP suggest a common emission source, i.e., e-

242 waste recycling practices.

243 The octanol-air partition coefficient (K_{OA}) is a useful descriptor for gas-particle partitioning[59].

244 While more volatile FRs with low K_{OA}s are anticipated to be present in the gaseous state, the

245 more in volatile chemicals (log K_{OA} > 12) are likely to be sorbed to particles if emitted into the air

246 [60]. We therefore estimated the log K_{OA} value at 30°C for most FRs studied (Table S2)[61-63] and

247 compared it with the measured distribution between gaseous and particulate fractions (Table S5).

248 In general, this comparison helped to explain the observed distribution for more volatile FRs. For

249 example, all FRs with an estimated log K_{OA} < 11 at 30°C were measured with at least twice as

250 large average concentrations in the PUFs compared to the filter, with the exception of TBB (log

251 K_{OA} at 30°C estimated at 11.67). On the other hand, the detection of in volatile chemicals (e.g.,

252 DBDPE) in the gaseous fraction is somewhat surprising and merits further investigation. The

253 concentrations of in volatile substances in PUFs cannot be excluded and, in part, may represent

254 an unintended signal from dust (a high concentration of $PM_{2.5}$), as previously observed in

255 passive air samples collected from different cities in Pakistan[34-36]. However, we note that the

256 uncertainties in K_{OA} may be considerable, particularly for the more in volatile and lesser studied

257 substances[63]. Furthermore, the K_{OA}-based model used to discuss anticipated gas-particle

258 partitioning is not universally accepted [64], and thus this study calls for further empirical studies

259 and more sophisticated models to better understand and evaluate gas-particle partitioning of FRs

260 in tropical source areas.

261 *∑PBDEs:* ∑PBDEs (gaseous+particulate) ranged from 40.0-275 ng/m^3 and exhibited the

262 following trend across sites: SS> JC > SJ > LY. Lower PBDEs, including BDE-28 (34.2 ng/m^3),

263 BDE-47 (29.0 ng/m^3) and BDE-99 (16.6 ng/m^3), were more prevalent than octa- and deca-BDEs

264 in atmospheric samples from Karachi (Figure 2), which in part may be explained by their

265 enhanced volatility and, therefore, abundance in the gaseous state relative to the more in volatile

266 PBDEs[65-66]. However, the average concentration of BDE-209 (12.0 ng/m^3) in this study was

267 higher than other studies that were conducted at e-waste sites. High concentrations have

268 previously been reported in samples from Guangzhou, China, with BDE-209 ranging from 0.26-

269 4.20 ng/m^3 [67]. Comparable levels from e-waste sites have been reported from Guiyu (1.95

270 ng/m^3)[68] and Taizhou (0.18 ng/m^3)[69]. The observed pattern of relatively high levels of volatile

271 PBDEs in the air, but not in soil, may be partly explained by a possible combined influence of

272 both primary and secondary sources[70-71]. A plausible explanation for the occurrence of lower

273 BDEs in the air is likely informal recycling activities of old electronic equipment containing

274 penta- and octa-BDE formulations, which were more extensively produced and used in the past.

275 Circuit boards contain relatively high portions of tetra- and penta-BDEs[72], and when these circuit

276 boards are grilled and melted for the recovery of valuable metals, lighter BDEs are emitted into

277 the atmosphere. The BDE-209 in waste may additionally be debrominated to lower and more

278 toxic PBDEs during the burning process of e-waste[72]. Therefore, the relatively high levels of

279 lower BDEs compared with BDE-209 in this study may be attributed to a combination of a) high

280 volatility of lower BDEs, b) primary and secondary sources, and c) debromination of BDE-209.

281 However, this requires further investigation. Our results confirm that e-waste recycling is a

282 significant emission source of lower brominated BDEs (di- through hexa-BDEs) to the

283 environment. All congeners were mostly prominent in the gaseous phase except BDE-99, BDE-

284 153 and BDE-154, which were mostly associated with the particulate phase.

285 *∑DP:* ∑DP was detected in both particulate and gaseous phases, but more than 70% was

286 detected in the particulate phase, which is consistent with previous studies by Hoh et al.[73], Wang

287 et al.[40] and Zhang et al.[42] and with theoretical expectations (log K_{OA} ~12 at 3°C)[63]. ∑DP

288 surrounding the manufacturing facility was comparable to levels in this study, with a mean of

289 26.7 ng/m^3 [40]. While data on DP in air from e-waste recycling sites remain scarce, the average

290 bulk concentration in air measured in this study (39.6 ng/m^3) is higher than what was previously

291 observed at an e-waste recycling site in China (0.36 ng/m^3) [74]. Lower levels have been reported

292 by various other studies in China close to DP manufacturing sites[40, 42] and urban centers[37, 75-76].

293 Studies from Pakistan also showed lower concentrations in the air from urban environments

294 close to River Ravi, River Chenab and Indus Basin, with concentrations as low as 0.09 ng/m^3,

295 0.0004 ng/m^3 and 0.0024 ng/m^3, respectively[34-36]. Most likely, the higher ∑DP concentrations in

296 the atmosphere found in this study may be attributed to the major application of commercial DP

297 in industrial polymers, which are used for coating electrical wires and cables, computer

298 connectors and plastic roofing material[41, 45]. Melting and open burning of wires and cables could

299   be a main cause of the high levels of DP measured in this study. For bulk air concentrations, *syn-*

300   DP ranged from 11.1-70.9 ng/m^3, while *anti*-DP ranged from 2.9-14.1 ng/m^3. Overall, the

301   concentrations of *syn*-DP were higher than *anti*-DP at all four sites. This is the opposite of

302   commercial DP products, where the fraction of anti-DP (*fanti*) dominates and is reported to vary

303   from 0.59-0.80[77]. In this study, *fanti* ranged between 0.04-0.28 in the air samples, with a mean of

304   0.15. Depletion of the anti-DP isomer in environmental samples has been reported earlier and

305   was attributed to either the enhanced stability of the *syn*-DP isomer towards photodegradation

306   and/or possible isomerization during atmospheric transport (from anti-DP to syn-DP)[77-78]. As our

307   measurements were taken in close proximity to e-waste sources, the results suggest that

308   weathering of the isomer profile compared to commercial mixtures may be a relatively rapid

309   process, which possibly influences the actual processing of e-waste. It is pertinent to mention

310   that there is no DP manufacturing plant in Pakistan. Hence, the presence of DP in the air is likely

311   attributable to two possible sources: e-waste recycling and LRAT from neighboring countries,

312   especially China. With regards to the latter, it has been previously suggested that differences in

313   relevant physical-chemical properties (K_{OA}) between the two isomers may additionally

314   contribute to more rapid relative depletion of *anti*-DP during LRAT[77, 79].

315   *∑OPFRs:* All investigated OPFRs (gaseous + particulate) were detected in the atmosphere of

316   Karachi: TPP (calculated as a sum of isomers; 7616 ng/m^3), TEHP (2251 ng/m^3) and TBP (2197

317   ng/m^3), which were the dominant OPFRs at all sites. Lyari showed the maximum concentration

318   of ∑OPFRs in air samples among all the sites, followed by SS, JC and SJ (Figure 2). The

319   ∑OPFRs concentration (particulate+gaseous) ranged from 5903 to 24986 (ng/m^3). ∑OPFRs in

320   Karachi's atmosphere were mainly distributed in the gaseous phase (Figure S6, Table S2), with a

321   mean gaseous associated fraction of 77.4% for ∑OPFRs and individual percentages ranging from

322 69% for TPP to 99% for TDCPP. There are limited data on the concentrations of OPFRs in

323 ambient air, especially from e-waste or other polluted areas. There have been a few studies

324 conducted in remote or non-urbanized regions that have reported low levels of OPFRs compared

325 to this study. A study on Norwegian arctic air reported low average levels of TBP (0.032–0.23

326 ng/m^3), TCEP (0.27 ng/m^3), TCPP (0.33 ng/m^3) and TDCP (0.087–0.25 ng/m^3) in remote air[80].

327 ∑OPFRs in the Arctic, North Sea and Great Lakes air were 1.50 ng/m^3, 0.369 ng/m^3 and 2.10

328 ng/m^3, respectively[81-83]. These studies suggest that there may be LRAT of OPFRs from source

329 regions to remote regions, such as the Arctic and the North Sea. In comparison to remote outdoor

330 environments, indoor environments typically experience much higher concentrations (by several

331 orders of magnitude), with levels of TCEP and TCPP up to 730 ng/m^3 and 570 ng/m^3,

332 respectively[84], which is still lower than the concentrations reported in this study (Tables S5 and

333 S6). Interestingly, Möller et al. (2012)[81] reported the highest concentrations of OPFRs near the

334 northern Indian Ocean and the Australian region, which suggested that major emissions occurred

335 in southeast Asian countries from production and that the use of OPFRs in Australia is

336 negligible[83] compared to extent urbanization and the use of OPFRs in countries such as China,

337 Pakistan and India. In this study, high levels of OPFRs measured in air suggest that informal e-

338 waste recycling activities in Karachi are a major hot-spot for atmospheric emissions. Future

339 studies should therefore try to elucidate the implications of atmospheric transport, occurrence

340 and distribution on a more regional scale. Given that informal recycling of e-waste occurs in

341 several East Asian countries, it cannot be ruled out that the observations made by Möller et al.

342 (2012) are partly explained by such activities[81].

343 *∑NBFRs:* DBDPE was the most abundant contaminant among the NBFRs in air, with an

344 average contribution of 61% and a mean concentration of 60.0 ng/m^3. The average

345 concentrations of other NBFRs (gaseous + particulate) were HBB (13.3 ng/m^3), TBB (12.9

346 ng/m^3), TBPH (6.10 ng/m^3), BTBPE (4.70 ng/m^3) and PBEB (2.30 ng/m^3). The levels of DBDPE

347 were higher than those of BDE-209, which, along with the soil results, suggest that informal

348 recycling of EEE has become a major source of DBDPE in Pakistan. Overall, the concentrations

349 of ΣNBFRs were higher in the gaseous phase (81%) (Figure S6), except for BTBPE (log K_{OA}

350 ~14.5, 41%). HBB (log K_{OA} 9.44) and PBEB (log K_{OA} 9.40) were most predominant in the

351 gaseous fraction among individual NBFRs, at 93% and 84%, respectively. The DBDPE level

352 reported from e-waste sites in Guangdong, China, was 1.91 ng/m^3, and 0.10 ng/m^3 was reported

353 at an e-waste site in South China[55, 85]. HBBs from e-waste sites in southern China had an average

354 concentration of 0.15 ng/m^3, while PBEBs from the same study reported an average

355 concentration as low as 0.08 ng/m^3[85]. Another study on e-waste sites in Taizhou, China reported

356 low levels of HBB (0.007 ng/m^3) and PBEB (6E-04 ng/m^3), with slightly higher levels of HBB

357 (0.01 ng/m^3) and PBEB (3E-04 ng/m^3) from historical e-waste sites[86]. These levels are minor in

358 comparison to the NBFRs measured in this study, which were higher than those in previous

359 studies of both urban and background ambient air[87-90]. However, studies of indoor dust from

360 electronic stores in Pakistan revealed higher levels of NBFRs than this study[91]. The levels of

361 indoor dust from electronic stores for TBB, TBPH, BTBPE and DBDPE were 3.0 ng/g, 100 ng/g,

362 1000 ng/g and 7100 ng/g, respectively[91]. High concentrations in the vicinity of e-waste recycling

363 sites in Karachi were therefore not surprising.

364 **3.3. Human exposure assessment**

365 Inhalation of contaminated air and ingestion of soil was hypothesized as possibly important

366 pathways for exposure to FRs among laborers at recycling sites. Various studies have

367 emphasized potential detrimental health effects following exposure to informal e-waste recycling

368　[7, 92]. Furthermore, concentrations of various FRs measured in human serum or breast milk have

369　previously been found to correlate with concentrations measured in hair and/or nails, which

370　indicates that inhalation and/or ingestion may be relevant exposure pathways[93-94]. Average doses

371　were calculated based on the assumption that laborers are directly exposed to contaminated air

372　and soil. Human exposure to environmental contaminants through the inhalation of outdoor air

373　and the ingestion of soil was estimated from average concentrations that we found in air and soil

374　samples across all sites through the application of inhalation and ingestion factors recommended

375　by the EPA[95]. RfD was taken for oral doses due to limited available data for inhalation RfDs.

376　RfDs used for the human exposure assessment are given in the SI (Table S4).

377　Average daily doses (ADD) and lifetime average doses from the air were calculated for FRs

378　analyzed in this study (Table S9). Air inhalation daily doses (gaseous + particulate) for OPFRs

379　(2334 ng/kg/day) were the highest among all the contaminants. PBDEs, DP, and NBFRs had

380　inhalation doses of 19.1, 5.42 and 13.7 ng/kg/day, respectively. Comparatively, inhalation of FRs

381　in this work was considerably lower than the RfD (reference dose) generated from toxicological

382　research and estimates provided by the EPA[96-97]. As predicted among individual sites, SS

383　displayed the highest levels of ADD for inhalation, with a value of 12087 ng/kg/day from a

384　combined mixture of FRs (NBFRs, PBDEs, DP and OPFRs), followed by LY (12051

385　ng/kg/day), JC (6166 ng/kg/day) and SJ (2876 ng/kg/day). These estimates are based on the

386　highest concentration of FRs measured in the air at each site. Since there is no RfD available for

387　mixtures of various FRs, the levels of ADD were compared with RfD (Table S4), which showed

388　that available RfD for OPFRs are comparatively higher than the RfD for BDEs. Therefore, the

389　inhalation risk for flame retardants was found to be low based on the quantified data. However,

390　RfD for inhalation exposures has not been developed for most of the FRs, which makes it

391 challenging to accurately predict the risk of exposure. Furthermore, the number of air samples

392 was limited and may not accurately reflect the concentrations that the workers were exposed to

393 during recycling activities. Nevertheless, in this study, exposure to ambient air due to inhalation

394 among laborers at e-waste recycling sites was less than previously reported inhalation from

395 indoor dust [57, 98].

396 Ingestion exposure was low compared to inhalation exposure; for all FRs combined, exposure for

397 ingestion was 3.94 ng/kg/day. Among individual FRs, *anti*-DP had the highest ingestion value of

398 1.9 ng/kg/day, followed by BDE-209, DBDPE and BTBPE, with values of 0.5 ng/kg/day, 0.38

399 ng/kg/day and 0.25 ng/kg/day, respectively. All other FRs showed negligible daily and lifetime

400 intake through soil ingestion. Among individual sites, SS displayed the highest values for ADD,

401 with a value of 15.69 ng/kg/day for all FRs combined. It should be noted that many uncertainties

402 are associated with exposure estimates that can affect the magnitude of exposure (personal

403 habits, dietary preferences, occupational settings, etc.). All FRs were well below the RfD, except

404 for DP, where values were lacking.

405 The results indicate that the average doses for these FRs in soil and air may increase if laborers

406 spend more time at the recycling sites than assumed herein. Furthermore, the recycling industry

407 in Karachi is expected to expand into other areas. Therefore, the possibility for increased

408 contamination of FRs exists, with increased exposure to laborers as well as nearby populations.

409 Further investigations considering additional contaminants and other exposure pathways are

410 needed to evaluate appropriate steps for more environmentally sound management of e-waste in

411 Karachi and Pakistan as a whole.

412 **3.4.   E-waste-driven pollution in Pakistan**

413   The concentrations of most FRs, as determined in both soil and air, were generally high, and the

414   spatial trends for these compounds indicate a role of informal e-waste processing as a major

415   potential source of FR emissions. Many informal activities at these sites are officially designated

416   dismantle and scrap yard activities. The spatial trends for PBDEs, NBFRs, DP and OPFRs, and

417   their inter-correlations, indicate common emission sources for these compounds, which may be

418   partially related to the release and/or formation from combustion processes such as the burning

419   of scrap materials, which is common in the studied e-waste sites. The presence of BDE-209 as

420   the major PBDE congener in soils around the sites indicates that e-waste originating from flame-

421   retardant products containing technical deca-BDE have been processed within Karachi. The

422   presence of emerging alternative FRs in the study area can be attributed to the fact that DBDPE

423   is used as an alternative for deca-BDEs, while TBB is used as a replacement for penta-BDE, an

424   additive FR in electronic goods. The high levels of NBFRs in the present study suggest the

425   replacement of legacy FRs at a large scale and the incorporation of NBFRs in EEE, which has

426   potentially important and significant implications for environmental and human exposure at

427   recycling sites in developing countries, such as Pakistan. Thus, the compositional trends of FRs

428   in this study area give us a clear indication of the replacement of legacy FRs with emerging FRs.

429   Pakistan is becoming one of the major e-waste destinations, with several hundred laborers

430   involved in this activity. With an e-waste generation increase of 5% from 2012-2014[5] and a 1.6%

431   population growth rate, Pakistan might be among one of the leading countries of e-waste

432   generation in the near future, which calls for regulatory efforts to minimize possibly harmful

433   impacts on environmental and human health. Our study confirms findings from other developing

434   countries, which implicate informal e-waste recycling activities as major potential emission

435   sources of FRs to the environment. Comparison with other studies from Pakistan shows e-waste

436 to be a primary cause of the high amounts of FRs in Karachi's environment. While the human

437 health risks associated with inhalation and soil ingestion of FRs are likely negligible, other

438 possible human exposure pathways merit further investigation (e.g., direct dermal contact and

439 diet). Future studies should also target exposures from a broader range of well-known toxins

440 either formed or released as a result of informal e-waste activities, such as PCBs, dioxins, PAHs

441 and various metals (e.g., mercury, lead, and cadmium). Given the increasing amount of e-waste

442 and expanding business for informal e-waste recycling in Pakistan, further research on this topic

443 could help inform and thereby support future regulatory efforts to minimize the negative impacts

444 of informal e-waste recycling on environmental and human health.

445 **Supplementary Information**

446 Description of sampling sites, meteorological conditions during the sampling period,

447 methodological details about the chemical analysis, statistical summaries of data, correlations

448 and estimated human exposures are given in the supplementary file. The supporting information

449 contains 19 pages, 9 tables and 6 figures.

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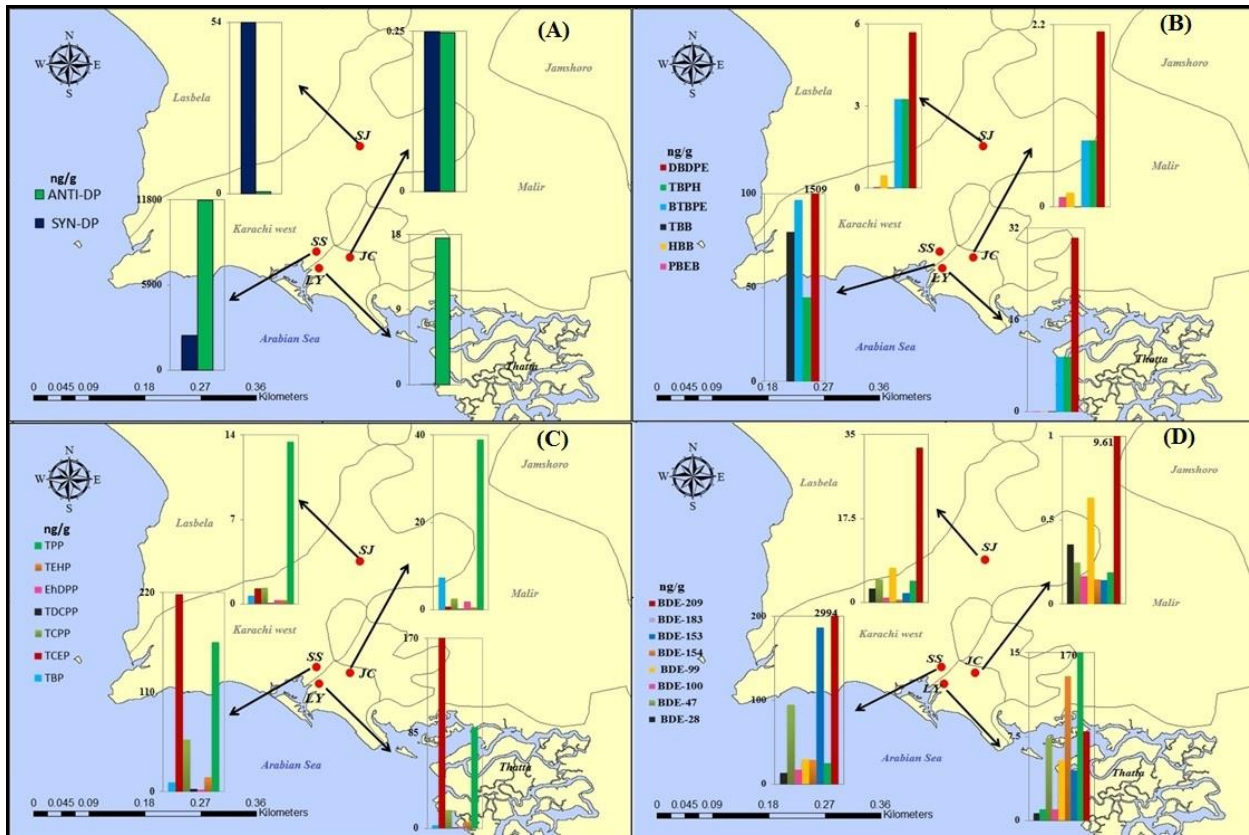
Figure 1: Spatial distribution of DP (A), NBFRs (B), OPFRs (C) and PBDEs (D) in the surface soils from e-waste sites
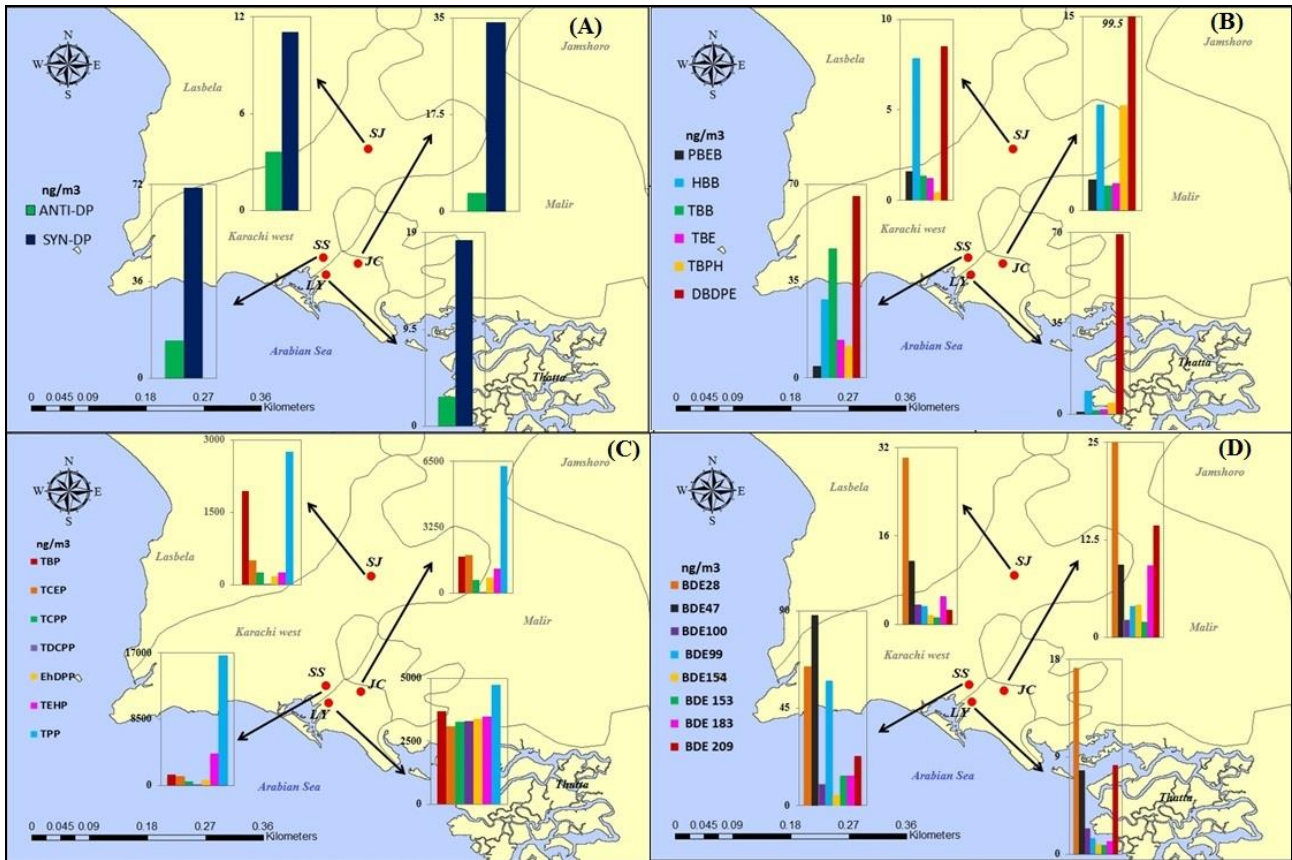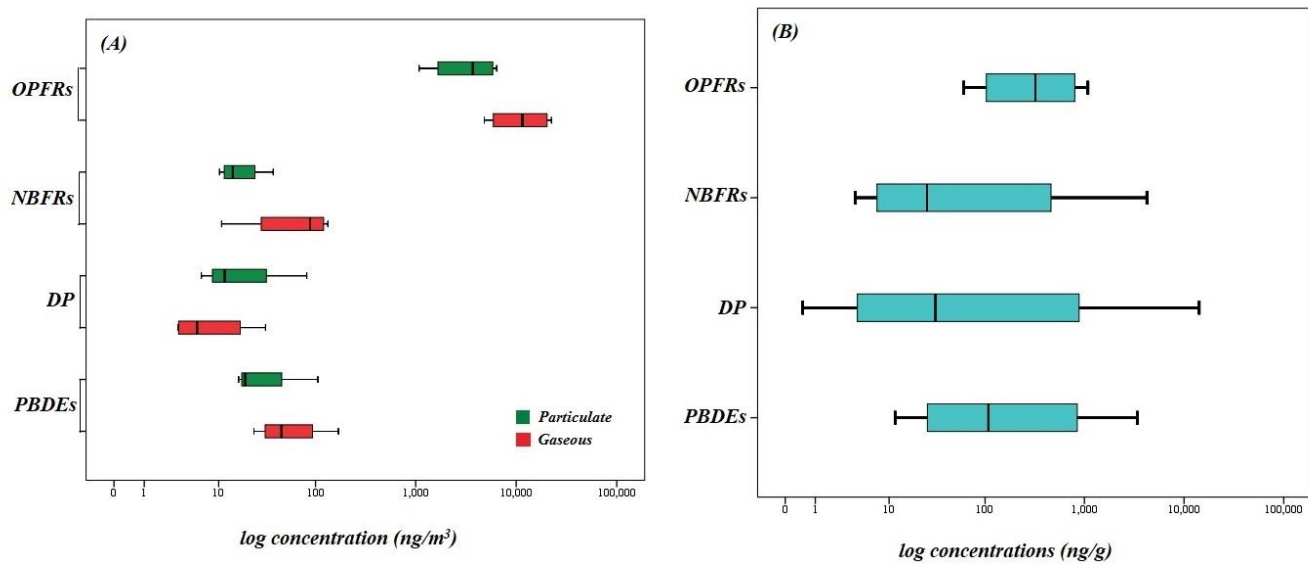
Figure 2: Spatial distribution of DP (A), NBFRs (B), OPFRs (C) and PBDEs (D) in the ambient air samples (particulate+gaseous) from e-waste sites

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Figure 3: Log concentrations of FRs in the atmosphere (A) and soil (B) of Karachi

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