

1 **Legacy and Emerging Flame Retardants (FRs) in the Urban Atmosphere of Pakistan:**
2 **Diurnal Variations, Gas-Particle Partitioning and Human Health Exposure**

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24 **Abstract**

25 Atmospheric concentration of legacy (LFRs) and emerging flame retardants (EFRs) including 8
26 polybrominated diphenyl ethers (PBDEs), 6 novel brominated flame retardants (NBFRs), 2
27 dechlorane plus isomers (DP), and 8 chlorinated organophosphate flame retardants (OPFRs) were

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<https://doi.org/10.1016/j.scitotenv.2020.140874>

28 consecutively measured in eight major cities across Pakistan. A total of 96 samples (48 PM_{2.5} &
29 48 PUFs) were analyzed and the concentrations of \sum_8 PBDEs (gaseous+particulate) ranged
30 between 40.8-288 pg/m³ with an average value of 172 pg/m³. \sum_6 NBFRs ranged between 12.0-35.0
31 pg/m³ with an average value of 22.5 pg/m³ while \sum_8 OPFRs ranged between 12,900-40,800 pg/m³
32 with an average of 24,700 pg/m³. Among the studied sites, Faisalabad city exhibited the higher
33 concentrations of FRs among all cities which might be a consequence of textile mills and garment
34 manufacturing industries. While analyzing the diurnal patterns, OPFRs depicted higher
35 concentrations during night-time. The estimated risks of all groups of FRs from inhalation of
36 ambient air were negligible for all the cities, according to USEPA guidelines. Nonetheless, our
37 study is the first to report gaseous and particulate concentrations of FRs in air on a diurnal basis
38 across major cities in Pakistan, offering insights into the atmospheric fate of these substances in
39 urban areas in a sub-tropical region.

40 **Keyword:** Flame retardants (FRs); urban atmosphere; diurnal variations; gas-particle partitioning;
41 human exposure

42 **1. Introduction**

43 Flame Retardants (FRs) have been extensively used for fire prevention in industrial and
44 commercial products such as plastics, textiles, polyurethane foams, wires, and cables for many
45 decades [1, 2]. Semi-volatile FRs have an enhanced potential to volatilize in warm regions, undergo
46 efficient atmospheric transport over long distances, and deposit more readily in remote cold
47 regions, such as the Arctic and high mountain areas[3, 4]. There are global concerns over
48 lipophilic, persistent and toxic FRs such as PBDEs [1, 5] (collectively referred to as “legacy” flame
49 retardants - LFRs) which have led to their banning or strict regulation all over the world under the
50 UNEP Stockholm Convention (SC) (Stockholm Convention, 2009). Among PBDEs, SC has

51 regulated the octa and penta BDE mixtures, while deca-BDE has been phased out in many
52 countries at the expense of novel brominated and phosphorous-based FRs (NBFRs & OPFRs) and
53 dechlorane plus (DP). Although these so-called ‘emerging’ FRs are not restricted for industrial
54 and commercial use, possess chemical structures similar to those of LFRs [6].
55 FRs, which typically have low vapor pressures and thereby high octanol–air partition coefficients
56 (K_{OA}), tend to bind to particulate matter and become more resistant to photo-degradation [7, 8].
57 Fine particulate matter ($PM_{2.5}$) has become a primary concern during the last decade especially in
58 developing world [9]. Various toxic materials and FRs associate with $PM_{2.5}$, which represents a
59 risk to human health [10]. Due to their carcinogenic and endocrine disrupting nature, persistence
60 and health impacts of different FRs such as PBDEs are of concern for both human and the
61 environment [11].

62 In the last decade, rapid economic development and industrialization in Pakistan have resulted in
63 a series of environmental problems. During past some years, studies have shown that major
64 Pakistani cities have been recorded with elevated levels of $PM_{2.5}$ which are resulting in adverse
65 effects on human health [12-18]. In addition, Pakistan has also been identified as major importer
66 of e-waste, which adds to a domestic e-waste generation of 317 kt in 2015 [19]. The unsafe and
67 non-ecofriendly practices for recycling of e-waste has become a challenge for Pakistan with no
68 registered formal recycling facilities. Previous studies conducted in the country have documented
69 wide-spread contamination of persistent organic pollutants [20-24]. Except for a few studies, [22,
70 25], information on atmospheric FRs (legacy/emerging) across the country remain insufficient and
71 incomplete. Hence, information on atmospheric levels of FRs across urban centers in Pakistan,
72 including sites with diverse geographic and weather conditions, are still lacking. In order to fill
73 the knowledge gap, this study was initiated to better understand the atmospheric levels, spatial and

74 diurnal variations and exposure of FRs in major cities of Pakistan. Beyond high population
75 densities and particulate pollution, atmospheric concentrations of FRs may also be influenced by
76 open burning of waste, uncontrolled industrial emissions and informal e-waste processing
77 activities in these areas. To our best of knowledge, this study presents the first data of gaseous and
78 particulate FRs in ambient air at such a large spatial scale in Pakistan.

79 **2. Materials & Methods**

80 **2.1. Sampling Details**

81 Outdoor air sampling was conducted in Karachi (KHI), Lahore (LHR), Faisalabad (FSD),
82 Rawalpindi (RWP), Multan (MLT), Quetta (QTA), Peshawar (PSH) and Gilgit (GLT)) (Figure
83 S1). Particulate (PM_{2.5}) and gaseous phase samples were collected using High Volume-Active Air
84 Sampler (Guangzhou Mingye Huanbao Technology Company) equipped with a PM_{2.5} inlet. All
85 samples were collected on the roof top of double story buildings (~10 m height). Air sampling
86 was performed with ~12 h intervals to reflect day (6am-6pm) and night (6pm-6am) times at a flow
87 of ~18m³/h. Samples were collected from the center of urban areas from all the cities. Further
88 details about sampling duration and sampling sites are illustrated in Supporting Information (SI)
89 (Table S1). Polyurethane foam (PUFs) (pre-extracted with acetone and hexane (48-h each)) and
90 quartz fiber filters (20×25 cm², 2600 QAT, PALL, USA; prebaked (450 °C, 6 h, muffle furnace),
91 were used to collect the gaseous and particulate phase respectively. A total of 96 samples (48 PM_{2.5}
92 & 48 PUFs) were analyzed for selected FRs from 8 sampling sites. Field blanks (5 PUFs & 5
93 filters) were also assembled in the active sampler (Turned OFF mode) at sampling sites, then
94 disassembled after approximately 5 minutes.

95 **2.2. Analysis of FRs**

96 The gravimetric weighing, pre-treatment and the chemical analysis used in this study are described
97 in SI (Section S1 &2). Chemical analyses were carried out for eight PBDEs: BDE-28, BDE-47,
98 BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 & BDE-209), six novel brominated flame
99 retardants (NBFRs: BEH-TBPH, PBEB, HBB, EH-TBB, BTBPE & DBDPE), eight
100 organophosphorus flame retardants (OPFRs: TCEP, TDCPP, TCPP (mixture of 3 isomers), TEHP,
101 TBP, TPHP, EHDPP, & TMPPs (mix of 3 isomers), and two dechlorane plus isomers (DP) (*anti*-
102 DP & *syn*-DP). See Table S2 for abbreviations. Description of further details of the experiments
103 can be found in the supporting information and elsewhere [26-28].

104 **2.3. QA/QC**

105 Strict quality assurance and quality control measures were followed for all analytical procedures.
106 To check any sample contamination and repeatability of the analyses, a procedural blank, a spiked
107 blank with all targeted compounds, and a duplicated sample were run with each batch of samples
108 (10 per batch). US EPA method 5055 (Table S2) was used to calculate the method detection limits
109 (MDLs). The MDLs were calculated as the average values of the field blanks plus 3 times the
110 standard deviation of the field blank values. In the case when a compound was not detected in the
111 field blank, the MDL for that compound was calculated as 3 times the instrumental detection limits
112 (IDLs). The IDLs were calculated from the lowest standards and extrapolated to the corresponding
113 amount of analyte that would generate a signal-to-noise ratio of 3:1.
114 None of the other compounds was detected in the procedural and laboratory blanks except for
115 BDE-209 (mean = 0.09 ng), TBP (mean = 0.91 ng) and TDCPP (mean = 0.07 ng). PCB-30, PCB-
116 198, PCB-209 and TCEP-d12 were used as recovery standards and their recoveries in all the
117 samples were accounted for $67\pm 14\%$, $72\pm 10\%$, $79\pm 19\%$ and $86\pm 9\%$, respectively. The results
118 were corrected based on recovery rates and blank values.

119 3. Results and discussion

120 3.1. Levels and Composition pattern of FRs

121 3.1.1. Polybrominated diphenyl ether (PBDEs)

122 A statistical summary of total air concentrations (gaseous phase + particulate phase) is presented
123 in Figure S2 and Table S3 whereas individual statistics of particulate and gaseous FRs in 8 major
124 cities in Pakistan are presented in Tables S4 & S5, respectively. PBDEs were frequently detected
125 in atmospheric samples. All PBDEs were detected in the particulate phase except for one sample
126 in Quetta (BDE-99) and one in Gilgit (BDE-209). For gaseous phase, BDE-153 was not detected
127 in 4 samples, BDE-183 in 2 samples and BDE-154 and BDE-99 were not detected in one sample
128 each. The concentrations of \sum_8 PBDEs (gaseous+particulate) at all sites were ranged between 40.8-
129 288 pg/m^3 with an average value of 172 pg/m^3 . These concentrations are higher than an earlier
130 study from 2013, using passive air samplers (PAS) nearby River Chenab (0.59-7.80 pg/m^3) [25],
131 Indus basin (1.43-22.1 pg/m^3) in 2012 [23], and River Ravi (8.20–12.0 pg/m^3) in 2011 [22]. It is
132 anticipated that this variation could be due to difference in sampling techniques and remoteness of
133 previous sampling sites from urban areas. Concentrations of \sum_8 PBDEs on particles in this study
134 ranged between 15.1-183 pg/m^3 while concentrations in the gas phase ranged between 25.7- 176
135 pg/m^3 .

136 Among individual BDE congeners, BDE-209 was the most prominent FR at almost all sites.
137 Concentrations of BDE-209 (gaseous+particulate) were in the range of 5.80-168 pg/m^3 with a
138 mean concentration of 91.6 pg/m^3 (Table S3). However, most of the BDE-209 were detected in
139 the particulate phase (>90%) (Figure 1) with an average value of 87.0 pg/m^3 and less in the gaseous
140 phase with average value of 4.60 pg/m^3 (Table S3). High concentrations of BDE-209 suggest that
141 emissions might have occurred in the vicinity, such as from current consumption and use of deca-

142 BDE in industrial and manufacturing processes or from e-waste recycling in the surroundings. The
143 second most abundant congener was BDE-28 which was mainly found in the PUFs (>70%; Figure
144 1) with an average concentration of 32.4 pg/m³ in the gaseous phase and 9.30 pg/m³ in the
145 particulate phase. The abundance of BDE-28 are consistent with results from Dalian (26.4 pg/m³)
146 [29] and Beijing (20.6 pg/m³) [30] cities of China. The other PBDE congeners associated with octa-
147 BDE and penta-BDE mixtures were generally found in lower quantities in all samples. The PBDEs
148 ranked as follows; BDE-209>BDE-28>BDE-47>BDE-100>BDE-99>BDE-183>BDE-
149 154>BDE-153. Typically, the relative fraction of PBDEs, other than BDE-209, detected on the
150 filter was ~50% or less, with lower brominated congener's being more abundant in gaseous phase
151 (Figure 1).

152 Compared to other countries (Figure S4), concentrations of BDE-28 in Pakistani cities were
153 comparable to Beijing [30], but higher than in Taiwan [31] and Harbin (2.50 pg/m³) [8]. However,
154 levels of BDE-28 from Pakistani urban centers were found to be higher and/or comparable to
155 measurements from other South Asian urban areas in India and Nepal [11, 32]. Concentrations of
156 BDE-209 in Pakistani cities are comparable to many Chinese cities and Khatmandu, Nepal [8, 9,
157 33] except one study from Guangzhou (China) where levels were much higher [34].

158 **3.1.2. Novel brominated flame retardants (NBFRs)**

159 The particulate and gaseous phase air samples were analyzed for six NBFRs. Σ_6 NBFRs in all cities
160 ranged between 12.0-35.0 pg/m³ with an average value of 22.5 pg/m³ (Table S3; Figure S2).
161 Among individual substances, DBDPE and HBB were most prominent whereas PBEB was
162 detected at high concentrations in a few samples. DBDPE, introduced in early 1990s, is now widely
163 used as a replacement of BDE-209 [35]. The bulk concentration of DBDPE across all sites varied
164 from 4.63 to 13.8 pg/m³, which is lower than BDE-209 (5.80-168 pg/m³). The average

165 concentration of DBDPE was 10.2 pg/m³ which was lower than that observed in Harbin (11.0
166 pg/m³)[8], rural China (158 pg/m³)[9] but higher than in Stockholm (0.15 pg/m³)[36] and Chicago
167 (1.50 pg/m³)[37] (Figure S4). HBB ranged from 2.50 to 13.6 pg/m³ across all sites and PBEB were
168 detected in the range of 0.60 – 9.00 pg/m³. HBB has been used as flame retardant in polymers,
169 plastics, textiles, woods and paper [37], and metal recycling facilities have been identified as
170 potential sources of HBB [38]. In our study, the mean concentration of HBB (7.40 pg/m³) were
171 comparable to Harbin city (4.80 pg/m³)[8], while higher than in Stockholm, Sweden[36] and
172 Chicago [37] (Figure S4). NBFRs, except DBDPE, were mostly found in gaseous phase while 85%
173 of DBDPE were found in particulate phase, attributed to a high K_{OA} (Figure 1).

174 **3.1.3 Organophosphate flame retardants (OPFRs)**

175 Overall levels of \sum_8 OPFRs across all cities ranged between 12,900 - 40,800 pg/m³ with an average
176 of 24,700 pg/m³, suggesting they are widely used in Pakistan. OPFRs were noticeable in the
177 particulate fraction of air samples (Table S3), which is consistent with previous studies [39, 40].
178 The mean concentrations of OPFRs were typically higher than other FRs (Table S3). These
179 elevated concentrations may be attributed to the fact that OPFRs are replacing other restricted FRs,
180 such as PBDEs. The global demand for OPFRs was reported to be 150,000 metric tons by
181 2010[41]. High concentrations have also been reported in urban areas of Japan where \sum OPFRs
182 ranged between 10,600-91,400 pg/m³[42]. High concentrations of \sum OPFRs have also been
183 reported near main roads in Norway (1,370-20,300 pg/m³)[43].
184 Among individual OPFRs, \sum TCPP was highest with an average value of 22023 pg/m³ (10,956-
185 37998 pg/m³). Levels of TPHP (12,000 pg/m³) have also been reported in Northern Finland[44].
186 \sum TMPP was the second most prominent OPFR, ranging between 555-1530 pg/m³ with an average
187 of 1032 pg/m³. Moller et al.[45] earlier reported a concentration of 1200 pg/m³ in the atmosphere

188 over the North Sea, comparable to this study. However studies from Finland (810 pg/m³)[44], Ny
189 Ålesund, Svalbard (330 pg/m³)[43], China (410 pg/m³)[27], Chicago (530 pg/m³) and Cleveland
190 (850 pg/m³) [46] reported lower concentrations of TMPP than measured in Pakistani cities. In the
191 present study, TEHP (572 pg/m³), TBP (520 pg/m³), EhDPP (279 pg/m³) and TCEP (276 pg/m³)
192 had lower concentrations in comparison to Σ TCPP and Σ TMPP. In general, our results show that
193 OPFRs are present in high concentrations in urban air in Pakistan.

194 **3.1.4. Dechlorane Plus (DP)**

195 DP is a highly chlorinated flame retardant which is used in coating wires/cables, plastic roofing
196 and textiles [47-49]. It is released into the environment via e-waste recycling practices, during
197 manufacturing as well as from use of products containing DP [50, 51]. In this study, *anti*-DP and
198 *syn*-DP were detected in all cities with concentrations ranging from 0.60-12.0 pg/m³ (3.08 pg/m³)
199 and 0.80-42.3 pg/m³ (10.8 pg/m³), respectively (Table S3). Σ DP ranged from 1.4-54.2 pg/m³ with
200 an average of 13.8 pg/m³. Past studies from Pakistan showed concentrations of Σ DP in urban air
201 in the vicinity to River Ravi, River Chenab and Indus Basin with levels of 88.0 pg/m³, 0.41 pg/m³
202 and 2.48 pg/m³, respectively [22, 23, 25]. Our results are comparable with a study in China where
203 the median level of Σ DP was 15.0 pg/m³[51]. A sampling cruise from the East Indian toward the
204 Indian Ocean and further to the Southern Ocean reported DP concentrations in the range of 0.26–
205 11.0 pg/m³ in the marine atmosphere [52], while a study from the Great Lakes, USA, showed
206 concentrations of DP ranging from 0.31-4.80 pg/m³ at an urban site in Chicago and 34.0 pg/m³ at
207 Sturgeon Point [49]. Another study from Sturgeon Point in 2005-2009 showed DP levels of 21.0
208 pg/m³ [53]. Vorkamp et al., 2015 reported mean air concentrations of *syn*- and *anti*-DP of 2.30 and
209 5.20 pg/m³ respectively, in Greenland [54]. A recent study from Chinese cities reported average
210 levels of 2.04 pg/m³ and 1.5 pg/m³ for *syn*-DP and *anti*-DP, respectively [27]. Apart from these

211 studies, high concentrations of DP have been reported in the surroundings of DP manufacturing
212 plants in many countries [50, 55]. Overall, the DP concentrations measured in this study compares
213 well with results reported elsewhere in the world.

214 The isomeric pattern of DP has been used to evaluate the transport and fate of DP in the atmosphere
215 [27]. In the present study, f_{anti} was calculated as the concentration of *anti*-DP divided by the sum
216 of the concentrations of *anti*-DP and *syn*-DP for each city. The f_{anti} values in this study ranged from
217 0.16 to 0.43 with a mean of 0.30, which is lower than those in DP commercial products Anpon
218 and OxyChem (0.60 and 0.80–0.64), respectively [50]. This pattern was similar to a recent study
219 from Chinese cities where f_{anti} ranged from 0.24 to 0.72 [27]. Low f_{anti} and *anti*-DP levels may be
220 attributed to the possible photo-degradation of *anti*-DP and/or isomerization from *anti*-DP to *syn*-
221 DP[27].

222 **3.2. Spatial and diurnal variations**

223 **3.2.1. Spatial Variations**

224 The spatial distributions of FRs in different Pakistani cities are presented in Figure 2. FSD
225 exhibited the highest concentrations of OPFRs, followed by LHR and RWP. Higher concentrations
226 in FSD and LHR are corroborated with a previous study, which also reported high concentrations
227 of some FRs such as PBDEs and DPs in same cities [22]. Comparatively, KHI, PSH and QTA
228 exhibited lower levels. Higher concentrations of PBDEs and NBFRs were observed in RWP which
229 might be due to the open burning of e-waste and other informal practices within commercial areas.
230 Average concentrations of \sum_8 PBDEs in RWP were 288 pg/m³, followed by LHR (238 pg/m³) and
231 PSH (214 pg/m³). RWP also showed the highest levels of \sum_6 NBFRs where levels were ranging
232 between 5.70-111 pg/m³, followed by FSD (8.40-40.3 pg/m³) and MLN (9.50-60.3 pg/m³). The
233 mean concentration of OPFRs was highest in FSD (40,801 pg/m³) followed by MLN (30,697

234 pg/m^3) and LHR (30,645 pg/m^3). The highest concentrations of DP were found in LHR with an
235 average concentration of 54.2 pg/m^3 , followed by KHI (13.9 pg/m^3) and QTA (13.0 pg/m^3).
236 Previous studies from major cities in Punjab Province have indicated contamination sources by
237 studied FRs [20, 22, 23, 25, 56]. In this study, sampling cities i.e., KHI, LHR, and FSD are hubs
238 of industrial activities in Pakistan [19, 22]. In these cities, large-scale production occurs which may
239 include use of FRs, e.g. in textiles, plastic products, small-scale manufacturing of electronics and
240 electrical equipment as well as preservatives. However, lower levels of FRs in samples from KHI
241 city might have been affected by specific meteorological conditions (sea breeze)[57]. Faisalabad
242 is known for textile mills and garment manufacturing industries[24] and this could be one possible
243 reason for the higher levels of FRs measured in this city. Additionally, e-waste recycling has been
244 identified as major contributing source of FRs to the atmosphere [19, 58]. Prevalence of OPFRs at
245 all sites might also be affected by their use as plasticizers, within wood and textiles industries, and
246 in vehicles [7, 44, 59].

247 3.2.2. Diurnal Variations

248 The diurnal variation in concentrations of FRs/POPs in air may be influenced by several factors.
249 Key processes include primary and secondary emissions, temperature, atmospheric reactions,
250 atmospheric transport and atmospheric mixing height (e.g. [60]). Therefore, diurnal variations of
251 FRs at a specific sampling site may provide insights about their atmospheric behavior and fate in
252 that environment. Figure 1 and Table S6 illustrate the diurnal variation of targeted FRs in
253 particulate and gaseous state. Overall, OPFRs tended to be slightly higher during nighttime, while
254 other FRs were mostly elevated during daytime. Increased anthropogenic activities and elevated
255 air temperatures during daytime potentially lead to enhanced emissions, which may result in higher
256 concentrations of FRs in air. TBP and TCPP showed higher concentrations during daytime (Figure

257 S3). Emissions and transport of OPFRs via the atmosphere from urban settlements and road traffic
258 has been proposed as a significant pathway into remote areas [44] and main roads [43]. As the
259 present study was conducted in urban settlements, a reason for high concentration of OPFRs might
260 be due to high traffic during night times because heavy-duty vehicles, such as loading trucks, are
261 permitted for driving at nighttime only at most of the national highways in Pakistan. Additionally,
262 a lower mixing height during night-time (i.e. a limited volume for “dilution”) and reduced potential
263 for atmospheric reaction (attributed to lower air temperatures and OH radical concentrations) may
264 also promote higher concentrations at night [61]. The latter effect is expected to be relatively more
265 influential for FRs with a short atmospheric half-life due to atmospheric reaction. When comparing
266 day-to-night ratios (Table S6), some OPFRs (TBP, TCEP, TCPP and TEHP) had a ratio of less
267 than one for total concentrations in air. These are also among those FRs which are estimated to
268 have a relatively short atmospheric half-life[62]. Interestingly, day-to-night ratios for all OPFRs
269 are smaller for gaseous concentrations in air, compared to particulate concentrations. Combined
270 with the relatively short half-lives for OPFRs, this suggests that atmospheric reaction during
271 daytime may be an important loss mechanism, affecting their diurnal variability. However, for
272 most PBDEs (except BDE209), *anti*DP and NBFRs (except TBPH and DBDPE), day-night ratios
273 tend to be the other way around (higher for gaseous concentrations). For these FRs, atmospheric
274 reaction during daytime may be of lesser significance controlling their diel variability, and/or
275 emissions/volatilization during daytime may be more important leading to higher concentrations.

276 3.3. Gas-Particle Partitioning

277 The distribution of FRs between sorbed and gaseous state affect their behavior and fate in the
278 atmosphere. Concentrations of FRs in both phases were determined to evaluate whether the
279 observed distribution could be rationalized from theoretical expectations. Table S6 shows

280 observed and predicted equilibrium partitioning onto aerosols, the latter based on K_{OA} [63, 64].
281 The K_{OA} -based equilibrium approach consistently underestimates the observed partitioning onto
282 aerosols for compounds with a $\log K_{OA}$ at 25°C < 11, and the other way around for FRs with a \log
283 K_{OA} at 25°C > 12 (Table S6). The poor agreement may in part be due to uncertainties in $\log K_{OA}$
284 [65], affecting these predictions. Furthermore, these results suggest a simple transition from “pure”
285 gaseous state towards “pure” sorbed state as function of K_{OA} alone may not always be accurate
286 [66]. For PBDEs, we have additionally included predictions based on a more recent steady-state
287 model, developed and recommended for this specific class of FRs by Li and co-workers [67]. For
288 most PBDEs (except BDE153), their steady-state model which include both an equilibrium and
289 non-equilibrium term, is in better agreement with the observed data than the equilibrium-based
290 approach (Table S6). A notable feature of their steady-state model is that PBDEs with high K_{OA}
291 tend to be more abundant in the gas phase, compared to the equilibrium model [68]. Using BDE-
292 209 as example [68], we have plotted the observed and predicted partitioning of BDE209 onto
293 aerosols for each individual sample, classified by site (Figure 3). While Li et al [68] has cautioned
294 their model may not be applicable for e-waste sites because of unpredictable emissions, sorption
295 of BDE-209 onto aerosols tend to be under-predicted by the steady-state model when confronted
296 with our measurements (69.4% vs 82.5% on average). One possible explanation for
297 underestimating the sorbed fraction, could be emissions of BDE-209 in sorbed state (e.g. dust
298 originating from physical abrasion / weathering of material containing BDE-209).

299 **3.4.Risk assessment due to inhalation of ambient air**

300 Human exposure to FRs from inhalation of outdoor air was estimated in the present study through
301 the application of the exposure factors provided by EPA [69, 70]. In this study, exposure was

302 assessed only via air inhalation in the outdoor environment. The average daily doses (ADD) of the
303 FRs by outdoor air were calculated using equation 1;

$$304 \quad \text{ADD} = C \times \text{IR} \times \text{ET}/\text{BW} \quad (1)$$

305 Where, C is the bulk concentration of FR in each sample (pg/m^3), IR is the inhalation rate
306 (m^3/hour), ET is the exposure time of an adult in outdoor environment (hours/day) and BW is body
307 weight of an adult (kg). A mean daily inhalation rate of $0.833 \text{ m}^3/\text{hour}$ was used with the
308 assumption that on average a person spends 6 h/day (i.e., 1/4 of the day) in an outdoor environment.
309 Average body weight was as assumed to be 70 kg. Due to limited studies of FRs in outdoor
310 environment, it was difficult to compare the ADD with previous studies, except a few on PBDEs
311 [21, 71]. Available Reference doses (RfD) (Table S7) in the literature were taken for the
312 comparisons with the results of estimated inhalation exposure.

313 The average ADD for NBFRs, PBDEs, DP and OPFRs were estimated as $1.61 \text{ pg}/\text{kg}\text{-BW}/\text{day}$,
314 $12.3 \text{ pg}/\text{kg}\text{-BW}/\text{day}$, $0.99 \text{ pg}/\text{kg}\text{-BW}/\text{day}$ and $1765 \text{ pg}/\text{kg}\text{-BW}/\text{day}$, respectively (Table S8).
315 Overall, the highest ADD was found for the samples from FSD, followed by LHR and MLT.
316 Earlier Fromme et al. reported an estimated ADD for outdoor air of BDE-209 for an average adult
317 in Germany, UK, and U.S. as 0.6, 0.6, and $0.3 \text{ pg}/\text{kg}\text{-BW}/\text{day}$ respectively [72]. He et al. estimated
318 ADDs for particulate BDE-209 ranging between $0.13\text{-}7.1 \text{ pg}/\text{kg}\text{-BW}/\text{day}$ (mean of $1.2 \text{ pg}/\text{kg}\text{-}$
319 BW/day) at an urban site in China [73]. Levels of BDE-209 in present study ($6.5 \text{ pg}/\text{kg}\text{-BW}/\text{day}$)
320 were lower than Guangzhou ($12 \text{ pg}/\text{kg}\text{-BW}/\text{day}$) [27].

321 In comparison to the similar studies and the RfD (reference dose) provided by EPA, the inhalation
322 risk in the present study is considerably lower [69, 70]. However, there is still a research need to
323 develop the RfDs for the rest of the FRs specially the NBFRs. It remains a challenge as of now to
324 accurately present the estimates of the risks posed by the FRs.

325 **4. Conclusions**

326 Our study is the first to report gaseous and particulate concentrations of FRs in air on a diurnal
327 basis across major cities in Pakistan, offering insights into the atmospheric fate of these substances
328 from eight (8) major urban areas in a sub-tropical region. We have discussed the atmospheric
329 levels, spatial and diurnal variations and health exposure of FRs, attributed with high population
330 densities and particulate matter pollution with insufficient e-waste processing and recycling
331 facilities in the country. Concentrations of studied FRs in this study are higher than previous
332 studies conducted in Pakistan. This could be due to differences in sampling techniques and/or
333 proximity to urban areas. While the observed diurnal variability differed across FRs studied,
334 concentrations of most FRs were generally higher during daytime. The predicted gas-particle
335 partitioning of individual PBDEs using a steady-state model was found to be in better agreements
336 with observations, compared with predictions using a simple equilibrium model. Higher
337 concentrations from industrialized urban areas showed that FRs emission is highly influenced by
338 industrial activities and informal e-waste recycling sites. Findings of health risk assessment due to
339 inhalation of air showed that inhalation of FRs was considerably lower than RfD (Reference dose)
340 generated from toxicological research and estimates provided by EPA. However, more data on
341 exposure pathways and toxicological data of emerging FRs, especially chlorinated OPFRs, are
342 urgently needed to enable an appropriate risk assessment.

343 **Supplementary Information**

344 The Supplementary Information contains the description of sampling sites, climatic parameters,
345 detailed chemical analysis, statistical summaries of data, correlations and estimated human
346 exposures. The supporting information contains 17 pages including supporting text, 8 tables and 3
347 figures.

348 **Acknowledgments**

349 We are grateful to Prof. Dr. Muhammad Arshad (Late), University of Agriculture Faisalabad
350 (UAF), Mr. Adeel Hassan Khan (Phd Scholar), Chinese Academy of Agricultural Sciences
351 (CAAS), Dr Azhar, Ms. Safia, Mr. Qurban and Mr. Nabeel, Karakoram International University
352 (KIU) and Mr. Bashir Ahmad and Mr. Junaid Khattak (Phd Scholar), Quaid-I-Azam University
353 (QAU) Islamabad for their kind assistance and support during sampling campaign.

354 **Funding**

355 This study is part of the CAS Belt & Road Initiative No. 132744KYSB20170002. We are very
356 thankful to Chinese Academy of Sciences (CAS) for PIFI (2015PE029) and NSFC grant
357 (41550110225). J.H.S. is also thankful to Pakistan Science Foundation (PSF) for PSF-
358 TUBITAK/Env/C-COMSATS-Isb (14). K.B. was supported by the Norwegian Research Council
359 [#213577, #267574].

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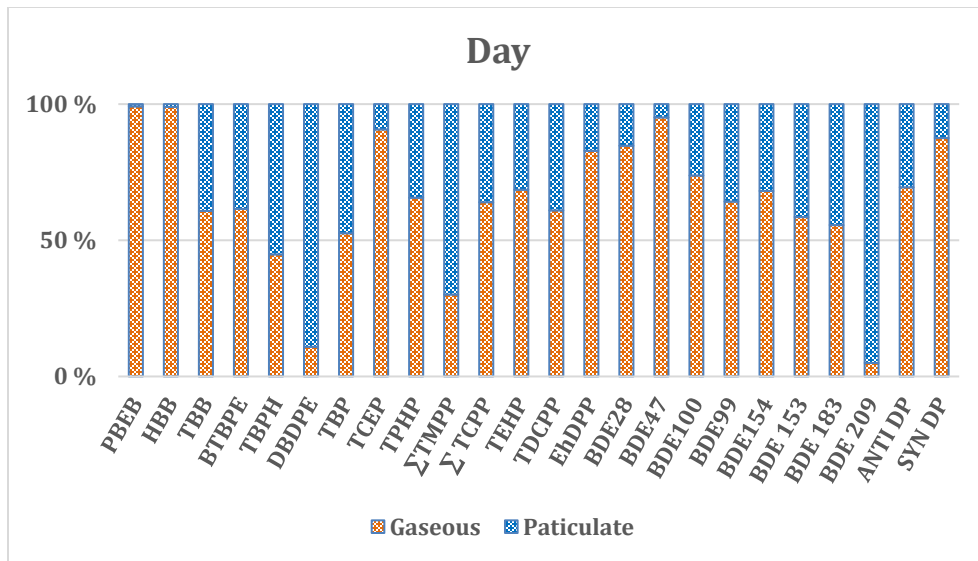
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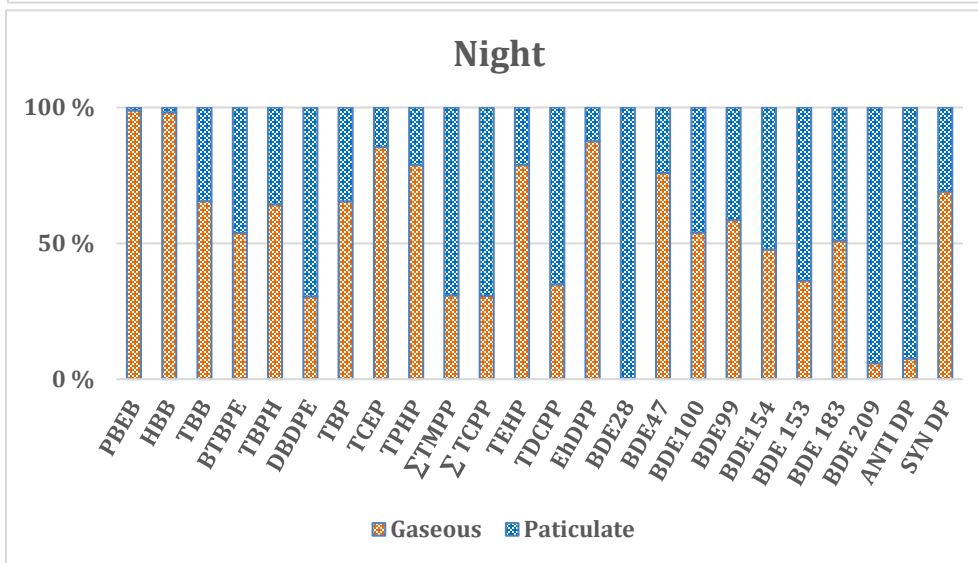
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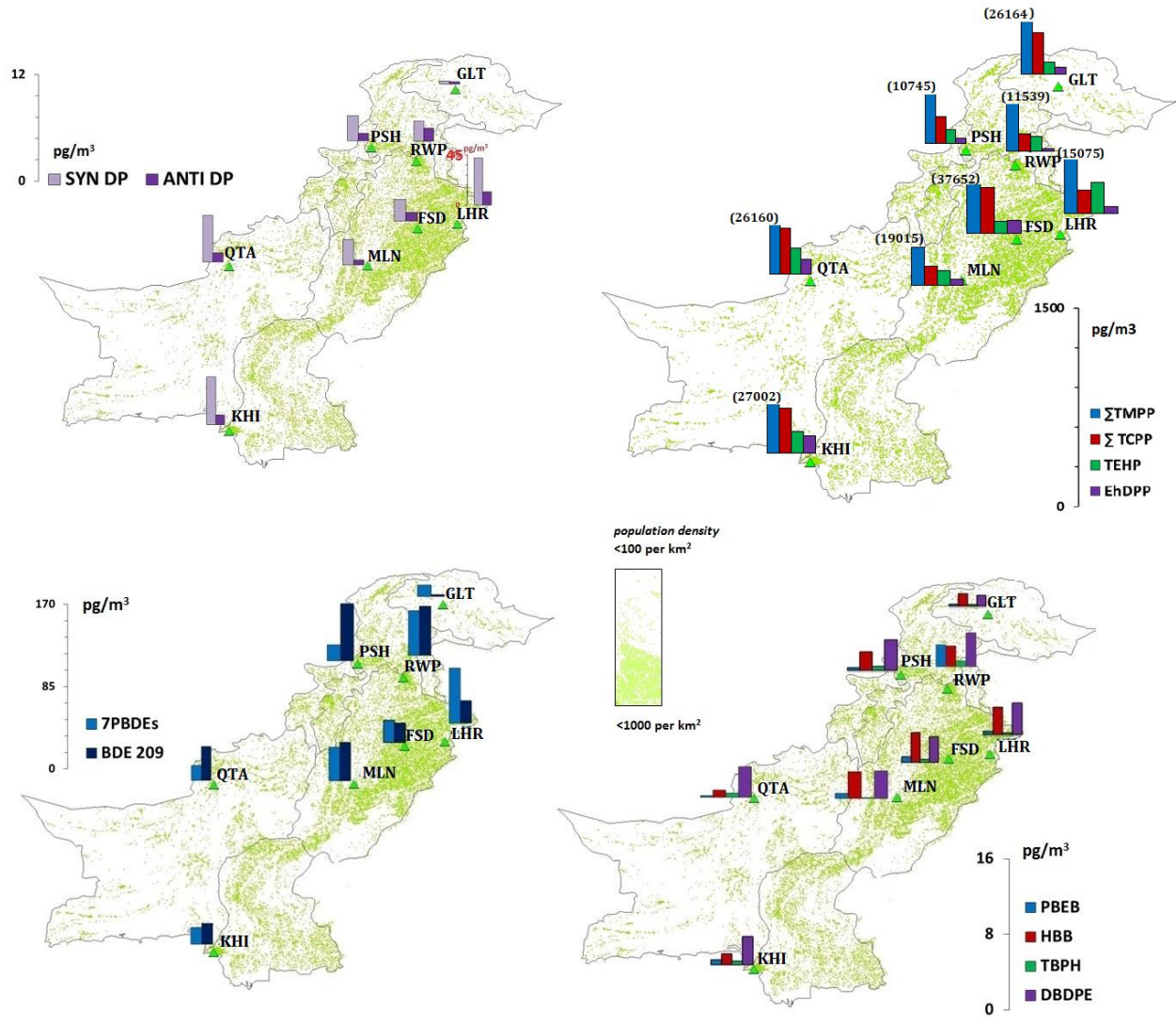
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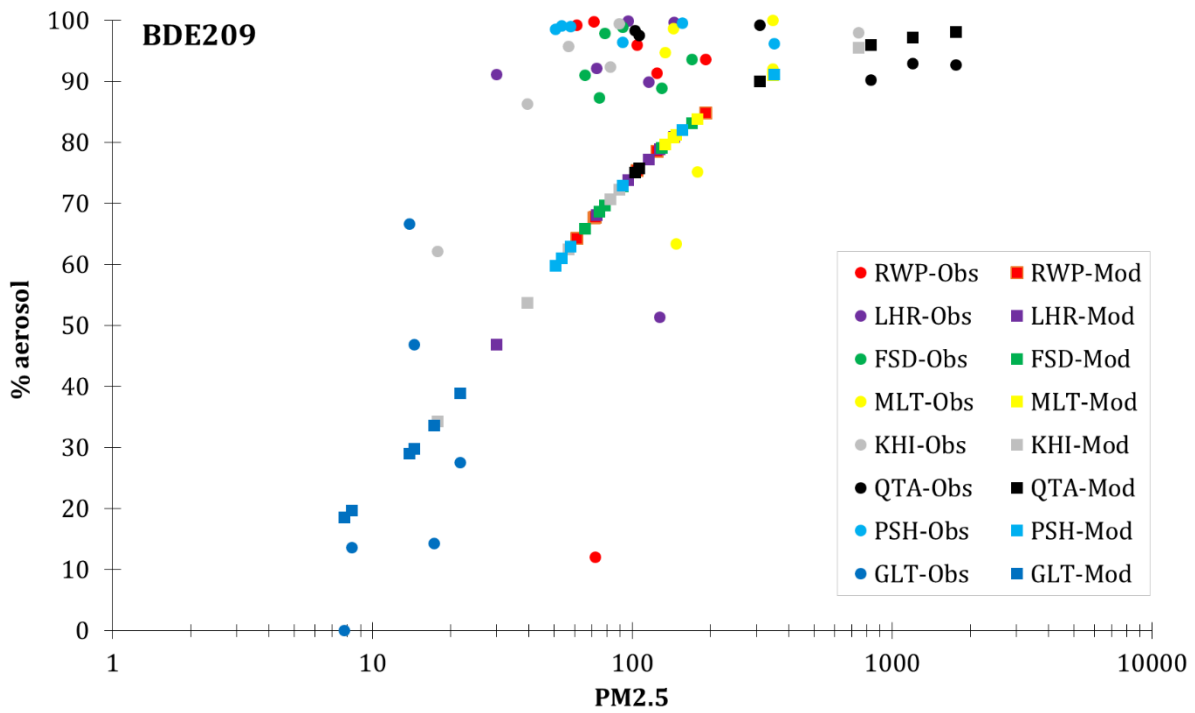
548 **Figure 1:** Relative distribution of FRs in gaseous and particulate phase for Day and Night

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550

551 **Figure 2:** Spatial distribution of FRs in air (gaseous+particulate) in 8 cities of Pakistan. Sum
 552 TMPP concentrations are shown in brackets



553

554 **Figure 3:** Observed (circles) and predicted (steady-state model, squares) partitioning of BDE209
 555 onto aerosols for each individual sample as function of PM_{2.5}, classified by site