

This is the preprint of the contribution published as:

Syed, J.H., **Iqbal, M.**, Breivik, K., Chaudhry, M.J.I., Shahnawaz, M., Abbas, Z., Nasir, J., Rizvi, S.H.H., Taqi, M.M., Li, J., Zhang, G. (2020):

Legacy and emerging flame retardants (FRs) in the urban atmosphere of Pakistan: Diurnal variations, gas-particle partitioning and human health exposure

Sci. Total Environ. **743** , art. 140874

The publisher's version is available at:

<http://dx.doi.org/10.1016/j.scitotenv.2020.140874>

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

Jabir Hussain Syed^{a,}, Mehreen Iqbal^{b,c}, Knut Breivik^{d,e}, Muhammad Jamshed Iqbal Chaudhry^f,
Muhammad Shahnawaz^g, Zaigham Abbas^h, Jawad Nasirⁱ, Syed Hussain Haider Rizvi^j, Malik
Mumtaz Taqi^j, Jun Li^k, Gan Zhang^k*

^aDepartment of Meteorology, COMSATS University Islamabad (CUI), Park Road, Tarlai Kalan,
Islamabad 45550 Pakistan

^bUFZ, Helmholtz Centre for Environmental Research, Department of Ecological Chemistry,
Permoserstrasse 15, 04318 Leipzig, Germany

^cInstitute of Organic Chemistry Technical University Bergakademie Freiberg, Leipziger Strasse
29, 09596 Freiberg, Germany

^dNorwegian Institute for Air Research, Box 100, NO-2027 Kjeller, Norway

^eUniversity of Oslo, Department of Chemistry, Box 1033, NO-0315 Oslo, Norway

^fWWF-Pakistan, Ferozpur Road, PO Box 5180, Lahore 54600, Pakistan

^gDepartment of Agriculture & Food Technology, Karakoram International University Main
Campus University Road Gilgit (15100) Pakistan

^hChemical Division, Ministry of Climate Change Islamabad, Pakistan

ⁱEarth Sciences Directorate, Pakistan Space and Upper Atmosphere Research Commission
(SUPARCO), P.O. Box 8402, Karachi 75270, Pakistan

^jNORMENT, University of Oslo, Norway

^kState Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese
Academy of Sciences, Guangzhou 510640, China

***Corresponding Author:** Jabir Hussain Syed, Ph.D.
Tel: (92-51) 9247000-3, **Fax:** (92-51) 9247006
Email: jabir.syed@comsats.edu.pk

Abstract

Atmospheric concentration of legacy (LFRs) and emerging flame retardants (EFRs) including 8
polybrominated diphenyl ethers (PBDEs), 6 novel brominated flame retardants (NBFRs), 2
dechlorane plus isomers (DP), and 8 chlorinated organophosphate flame retardants (OPFRs) were
consecutively measured in eight major cities across Pakistan. A total of 96 samples (48 PM_{2.5} &

48 PUFs) were analyzed and the concentrations of Σ_8 PBDEs (gaseous+particulate) ranged between 40.8-288 pg/m³ with an average value of 172 pg/m³. Σ_6 NBFRs ranged between 12.0-35.0 pg/m³ with an average value of 22.5 pg/m³ while Σ_8 OPFRs ranged between 12,900-40,800 pg/m³ with an average of 24,700 pg/m³. Among the studied sites, Faisalabad city exhibited the higher concentrations of FRs among all cities which might be a consequence of textile mills and garment manufacturing industries. While analyzing the diurnal patterns, OPFRs depicted higher concentrations during night-time. The estimated risks of all groups of FRs from inhalation of ambient air were negligible for all the cities, according to USEPA guidelines. Nonetheless, our study is the first to report gaseous and particulate concentrations of FRs in air on a diurnal basis across major cities in Pakistan, offering insights into the atmospheric fate of these substances in urban areas in a sub-tropical region.

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

1. Introduction

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

countries at the expense of novel brominated and phosphorous-based FRs (NBFRs & OPFRs) and dechlorane plus (DP). Although these so-called ‘emerging’ FRs are not restricted for industrial and commercial use, possess chemical structures similar to those of LFRs [6].

FRs, which typically have low vapor pressures and thereby high octanol–air partition coefficients (K_{OA}), tend to bind to particulate matter and become more resistant to photo-degradation [7, 8]. Fine particulate matter ($PM_{2.5}$) has become a primary concern during the last decade especially in developing world [9]. Various toxic materials and FRs associate with $PM_{2.5}$, which represents a risk to human health [10]. Due to their carcinogenic and endocrine disrupting nature, persistence and health impacts of different FRs such as PBDEs are of concern for both human and the environment [11].

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

densities and particulate pollution, atmospheric concentrations of FRs may also be influenced by open burning of waste, uncontrolled industrial emissions and informal e-waste processing activities in these areas. To our best of knowledge, this study presents the first data of gaseous and particulate FRs in ambient air at such a large spatial scale in Pakistan.

2. Materials & Methods

2.1. Sampling Details

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

2.2. Analysis of FRs

The gravimetric weighing, pre-treatment and the chemical analysis used in this study are described in SI (Section S1 &2). Chemical analyses were carried out for eight PBDEs: BDE-28, BDE-47,

BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 & BDE-209), six novel brominated flame retardants (NBFRs: BEH-TBPH, PBEB, HBB, EH-TBB, BTBPE & DBDPE), eight organophosphorus flame retardants (OPFRs: TCEP, TDCPP, TCPP (mixture of 3 isomers), TEHP, TBP, TPHP, EHDPP, & TMPPs (mix of 3 isomers), and two dechlorane plus isomers (DP) (*anti*-DP & *syn*-DP). See Table S2 for abbreviations. Description of further details of the experiments can be found in the supporting information and elsewhere [26-28].

2.3. QA/QC

Strict quality assurance and quality control measures were followed for all analytical procedures. To check any sample contamination and repeatability of the analyses, a procedural blank, a spiked blank with all targeted compounds, and a duplicated sample were run with each batch of samples (10 per batch). US EPA method 5055 (Table S2) was used to calculate the method detection limits (MDLs). The MDLs were calculated as the average values of the field blanks plus 3 times the standard deviation of the field blank values. In the case when a compound was not detected in the field blank, the MDL for that compound was calculated as 3 times the instrumental detection limits (IDLs). The IDLs were calculated from the lowest standards and extrapolated to the corresponding amount of analyte that would generate a signal-to-noise ratio of 3:1.

None of the other compounds was detected in the procedural and laboratory blanks except for BDE-209 (mean = 0.09 ng), TBP (mean = 0.91 ng) and TDCPP (mean = 0.07 ng). PCB-30, PCB-198, PCB-209 and TCEP-d12 were used as recovery standards and their recoveries in all the samples were accounted for 67±14%, 72±10%, 79±19% and 86±9%, respectively. The results were corrected based on recovery rates and blank values.

3. Results and discussion

3.1. Levels and Composition pattern of FRs

3.1.1. Polybrominated diphenyl ether (PBDEs)

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

Among individual BDE congeners, BDE-209 was the most prominent FR at almost all sites. Concentrations of BDE-209 (gaseous+particulate) were in the range of 5.80-168 pg/m^3 with a mean concentration of 91.6 pg/m^3 (Table S3). However, most of the BDE-209 were detected in the particulate phase (>90%) (Figure 1) with an average value of 87.0 pg/m^3 and less in the gaseous phase with average value of 4.60 pg/m^3 (Table S3). High concentrations of BDE-209 suggest that emissions might have occurred in the vicinity, such as from current consumption and use of deca-BDE in industrial and manufacturing processes or from e-waste recycling in the surroundings. The second most abundant congener was BDE-28 which was mainly found in the PUFs (>70%; Figure

1) with an average concentration of 32.4 pg/m³ in the gaseous phase and 9.30 pg/m³ in the particulate phase. The abundance of BDE-28 are consistent with results from Dalian (26.4 pg/m³) [29] and Beijing (20.6 pg/m³) [30] cities of China. The other PBDE congeners associated with octa-BDE and penta-BDE mixtures were generally found in lower quantities in all samples. The PBDEs ranked as follows; BDE-209>BDE-28>BDE-47>BDE-100>BDE-99>BDE-183>BDE-154>BDE-153. Typically, the relative fraction of PBDEs, other than BDE-209, detected on the filter was ~50% or less, with lower brominated congener's being more abundant in gaseous phase (Figure 1).

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

3.1.2. *Novel brominated flame retardants (NBFRs)*

The particulate and gaseous phase air samples were analyzed for six NBFRs. \sum_6 NBFRs in all cities ranged between 12.0-35.0 pg/m³ with an average value of 22.5 pg/m³ (Table S3; Figure S2). Among individual substances, DBDPE and HBB were most prominent whereas PBEB was detected at high concentrations in a few samples. DBDPE, introduced in early 1990s, is now widely used as a replacement of BDE-209 [35]. The bulk concentration of DBDPE across all sites varied from 4.63 to 13.8 pg/m³, which is lower than BDE-209 (5.80-168 pg/m³). The average concentration of DBDPE was 10.2 pg/m³ which was lower than that observed in Harbin (11.0 pg/m³) [8], rural China (158 pg/m³) [9] but higher than in Stockholm (0.15 pg/m³) [36] and Chicago

(1.50 pg/m³)[37] (Figure S4). HBB ranged from 2.50 to 13.6 pg/m³ across all sites and PBEB were detected in the range of 0.60 – 9.00 pg/m³. HBB has been used as flame retardant in polymers, plastics, textiles, woods and paper [37], and metal recycling facilities have been identified as potential sources of HBB [38]. In our study, the mean concentration of HBB (7.40 pg/m³) were comparable to Harbin city (4.80 pg/m³)[8], while higher than in Stockholm, Sweden[36] and Chicago [37] (Figure S4). NBRs, except DBDPE, were mostly found in gaseous phase while 85% of DBDPE were found in particulate phase, attributed to a high K_{OA} (Figure 1).

3.1.3 *Organophosphate flame retardants (OPFRs)*

Overall levels of \sum_8 OPFRs across all cities ranged between 12,900 - 40,800 pg/m³ with an average of 24,700 pg/m³, suggesting they are widely used in Pakistan. OPFRs were noticeable in the particulate fraction of air samples (Table S3), which is consistent with previous studies [39, 40]. The mean concentrations of OPFRs were typically higher than other FRs (Table S3). These elevated concentrations may be attributed to the fact that OPFRs are replacing other restricted FRs, such as PBDEs. The global demand for OPFRs was reported to be 150,000 metric tons by 2010[41]. High concentrations have also been reported in urban areas of Japan where \sum OPFRs ranged between 10,600-91,400 pg/m³[42]. High concentrations of \sum OPFRs have also been reported near main roads in Norway (1,370-20,300 pg/m³)[43].

Among individual OPFRs, \sum TCPP was highest with an average value of 22023 pg/m³ (10,956-37998 pg/m³). Levels of TPHP (12,000 pg/m³) have also been reported in Northern Finland[44]. \sum TMPP was the second most prominent OPFR, ranging between 555-1530 pg/m³ with an average of 1032 pg/m³. Moller et al.[45] earlier reported a concentration of 1200 pg/m³ in the atmosphere over the North Sea, comparable to this study. However studies from Finland (810 pg/m³)[44], Ny Ålesund, Svalbard (330 pg/m³)[43], China (410 pg/m³)[27], Chicago (530 pg/m³) and Cleveland

(850 pg/m³) [46] reported lower concentrations of TMPP than measured in Pakistani cities. In the present study, TEHP (572 pg/m³), TBP (520 pg/m³), EhDPP (279 pg/m³) and TCEP (276 pg/m³) had lower concentrations in comparison to Σ TCPP and Σ TMPP. In general, our results show that OPFRs are present in high concentrations in urban air in Pakistan.

3.1.4. Dechlorane Plus (DP)

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

plants in many countries [50, 55]. Overall, the DP concentrations measured in this study compares well with results reported elsewhere in the world.

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

3.2. Spatial and diurnal variations

3.2.1. Spatial Variations

The spatial distributions of FRs in different Pakistani cities are presented in Figure 2. FSD exhibited the highest concentrations of OPFRs, followed by LHR and RWP. Higher concentrations in FSD and LHR are corroborated with a previous study, which also reported high concentrations of some FRs such as PBDEs and DPs in same cities [22]. Comparatively, KHI, PSH and QTA exhibited lower levels. Higher concentrations of PBDEs and NBFRs were observed in RWP which might be due to the open burning of e-waste and other informal practices within commercial areas. Average concentrations of \sum_8 PBDEs in RWP were 288 pg/m³, followed by LHR (238 pg/m³) and PSH (214 pg/m³). RWP also showed the highest levels of \sum_6 NBFRs where levels were ranging between 5.70-111 pg/m³, followed by FSD (8.40-40.3 pg/m³) and MLN (9.50-60.3 pg/m³). The mean concentration of OPFRs was highest in FSD (40,801 pg/m³) followed by MLN (30,697 pg/m³) and LHR (30,645 pg/m³). The highest concentrations of DP were found in LHR with an

average concentration of 54.2 pg/m³, followed by KHI (13.9 pg/m³) and QTA (13.0 pg/m³). Previous studies from major cities in Punjab Province have indicated contamination sources by studied FRs [20, 22, 23, 25, 56]. In this study, sampling cities i.e., KHI, LHR, and FSD are hubs of industrial activities in Pakistan [19, 22]. In these cities, large-scale production occurs which may include use of FRs, e.g. in textiles, plastic products, small-scale manufacturing of electronics and electrical equipment as well as preservatives. However, lower levels of FRs in samples from KHI city might have been affected by specific meteorological conditions (sea breeze)[57]. Faisalabad is known for textile mills and garment manufacturing industries[24] and this could be one possible reason for the higher levels of FRs measured in this city. Additionally, e-waste recycling has been identified as major contributing source of FRs to the atmosphere [19, 58]. Prevalence of OPFRs at all sites might also be affected by their use as plasticizers, within wood and textiles industries, and in vehicles [7, 44, 59].

3.2.2. Diurnal Variations

The diurnal variation in concentrations of FRs/POPs in air may be influenced by several factors. Key processes include primary and secondary emissions, temperature, atmospheric reactions, atmospheric transport and atmospheric mixing height (e.g. [60]). Therefore, diurnal variations of FRs at a specific sampling site may provide insights about their atmospheric behavior and fate in that environment. Figure 1 and Table S6 illustrate the diurnal variation of targeted FRs in particulate and gaseous state. Overall, OPFRs tended to be slightly higher during nighttime, while other FRs were mostly elevated during daytime. Increased anthropogenic activities and elevated air temperatures during daytime potentially lead to enhanced emissions, which may result in higher concentrations of FRs in air. TBP and TCPP showed higher concentrations during daytime (Figure S3). Emissions and transport of OPFRs via the atmosphere from urban settlements and road traffic

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

3.3. Gas-Particle Partitioning

The distribution of FRs between sorbed and gaseous state affect their behavior and fate in the atmosphere. Concentrations of FRs in both phases were determined to evaluate whether the observed distribution could be rationalized from theoretical expectations. Table S6 shows observed and predicted equilibrium partitioning onto aerosols, the latter based on K_{OA} [63, 64].

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

3.4.Risk assessment due to inhalation of ambient air

Human exposure to FRs from inhalation of outdoor air was estimated in the present study through the application of the exposure factors provided by EPA [69, 70]. In this study, exposure was assessed only via air inhalation in the outdoor environment. The average daily doses (ADD) of the FRs by outdoor air were calculated using equation 1;

$$ADD = C \times IR \times ET/BW \quad (1)$$

Where, C is the bulk concentration of FR in each sample (pg/m³), IR is the inhalation rate (m³/hour), ET is the exposure time of an adult in outdoor environment (hours/day) and BW is body weight of an adult (kg). A mean daily inhalation rate of 0.833 m³/hour was used with the assumption that on average a person spends 6 h/day (i.e., 1/4 of the day) in an outdoor environment. Average body weight was as assumed to be 70 kg. Due to limited studies of FRs in outdoor environment, it was difficult to compare the ADD with previous studies, except a few on PBDEs [21, 71]. Available Reference doses (RfD) (Table S7) in the literature were taken for the comparisons with the results of estimated inhalation exposure.

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

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

4. Conclusions

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

Supplementary Information

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

Acknowledgments

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

Funding

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

References

1. Luo, P., et al., *Health risk characterization for resident inhalation exposure to particle-bound halogenated flame retardants in a typical e-waste recycling zone*. Environmental science & technology, 2014. **48**(15): p. 8815-8822.
2. Matsukami, H., et al., *Flame retardant emission from e-waste recycling operation in northern Vietnam: Environmental occurrence of emerging organophosphorus esters used as alternatives for PBDEs*. Science of The Total Environment, 2015. **514**: p. 492-499.
3. Kallenborn, R., H. Hung, and E. Brorström-Lundén, *Atmospheric long-range transport of persistent organic pollutants (POPs) into polar regions*, in *Comprehensive Analytical Chemistry*. 2015, Elsevier. p. 411-432.
4. de Wit, C.A., D. Herzke, and K. Vorkamp, *Brominated flame retardants in the Arctic environment—trends and new candidates*. Science of the Total Environment, 2010. **408**(15): p. 2885-2918.
5. Tao, F., et al., *Emerging halogenated flame retardants and hexabromocyclododecanes in food samples from an e-waste processing area in Vietnam*. Environmental Science: Processes & Impacts, 2016.
6. Covaci, A., et al., *Novel brominated flame retardants: a review of their analysis, environmental fate and behaviour*. 2011. **37**(2): p. 532-556.
7. Van der Veen, I. and J. de Boer, *Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis*. Chemosphere, 2012. **88**(10): p. 1119-1153.
8. Qi, H., et al., *Brominated flame retardants in the urban atmosphere of Northeast China: Concentrations, temperature dependence and gas-particle partitioning*. Science of the Total Environment, 2014. **491**: p. 60-66.

9. Tian, M., et al., *Brominated flame retardants in the atmosphere of e-waste and rural sites in southern China: Seasonal variation, temperature dependence, and gas-particle partitioning*. Environmental science & technology, 2011. **45**(20): p. 8819-8825.
10. Zhang, A., et al., *Population exposure to PM 2.5 in the urban area of Beijing*. PloS one, 2013. **8**(5): p. e63486.
11. Chakraborty, P., et al., *PCBs and PCDD/Fs in soil from informal e-waste recycling sites and open dumpsites in India: levels, congener profiles and health risk assessment*. Science of the Total Environment, 2018. **621**: p. 930-938.
12. Hameed, S., et al., *On the widespread winter fog in northeastern Pakistan and India*. Geophysical Research Letters, 2000. **27**(13): p. 1891-1894.
13. Husain, L., et al., *Characterization of carbonaceous aerosols in urban air*. Atmospheric Environment, 2007. **41**(32): p. 6872-6883.
14. Alam, K., et al., *Source apportionment and characterization of particulate matter (PM10) in urban environment of Lahore*. Aerosol Air Qual. Res, 2014. **14**(7): p. 1851-1861.
15. Shahid, M.Z., et al., *Seasonal variations of aerosols in Pakistan: Contributions of domestic anthropogenic emissions and transboundary transport*. Aerosol Air Qual. Res, 2015. **15**: p. 1580-1600.
16. Lodhi, A., et al., *Particulate matter (PM2. 5) concentration and source apportionment in Lahore*. Journal of the Brazilian Chemical Society, 2009. **20**(10): p. 1811-1820.
17. Mansha, M., et al., *Characterization and source apportionment of ambient air particulate matter (PM 2.5) in Karachi*. Science of the total environment, 2012. **425**: p. 176-183.
18. Rasheed, A., et al., *Measurement and analysis of fine particulate matter (PM2. 5) in urban areas of Pakistan*. Aerosol Air Qual. Res, 2015. **15**: p. 426-439.
19. Iqbal, M., et al., *Emerging issue of e-waste in Pakistan: A review of status, research needs and data gaps*. Environmental Pollution, 2015. **207**: p. 308-318.
20. Ali, N., et al., *Levels and profile of several classes of organic contaminants in matched indoor dust and serum samples from occupational settings of Pakistan*. Environmental Pollution, 2014. **193**: p. 269-276.
21. Ali, N., et al., *Levels and profiles of organochlorines and flame retardants in car and house dust from Kuwait and Pakistan: implication for human exposure via dust ingestion*. Environment international, 2013. **55**: p. 62-70.
22. Syed, J.H., et al., *Levels, profile and distribution of Dechloran Plus (DP) and Polybrominated Diphenyl Ethers (PBDEs) in the environment of Pakistan*. Chemosphere, 2013. **93**(8): p. 1646-1653.
23. Ali, U., et al., *Assessing the combined influence of TOC and black carbon in soil–air partitioning of PBDEs and DPs from the Indus River Basin, Pakistan*. Environmental Pollution, 2015. **201**: p. 131-140.
24. Khan, M.U., et al., *First insight into the levels and distribution of flame retardants in potable water in Pakistan: An underestimated problem with an associated health risk diagnosis*. Science of The Total Environment, 2016. **565**: p. 346-359.
25. Mahmood, A., et al., *Dietary exposure and screening-level risk assessment of polybrominated diphenyl ethers (PBDEs) and dechloran plus (DP) in wheat, rice, soil and air along two tributaries of the River Chenab, Pakistan*. Chemosphere, 2015. **118**: p. 57-64.
26. Iqbal, M., et al., *E-waste driven pollution in Pakistan: the first evidence of environmental and human exposure to flame retardants (FRs) in Karachi City*. Environmental science & technology, 2017. **51**(23): p. 13895-13905.
27. Liu, D., et al., *Occurrence and concentrations of halogenated flame retardants in the atmospheric fine particles in Chinese Cities*. Environmental Science & Technology, 2016.

28. Yadav, I.C., et al., *Organophosphate ester flame retardants in Nepalese soil: spatial distribution, source apportionment and air-soil exchange assessment*. Chemosphere, 2018. **190**: p. 114-123.
29. Yang, M., et al., *Levels, compositions, and gas-particle partitioning of polybrominated diphenyl ethers and dechlorane plus in air in a Chinese northeastern city*. Atmospheric environment, 2012. **55**: p. 73-79.
30. Yang, M., et al., *Polybrominated diphenyl ethers in air across China: levels, compositions, and gas-particle partitioning*. Environmental science & technology, 2013. **47**(15): p. 8978-8984.
31. Gou, Y.-Y., et al., *Pollution characteristics and diurnal variations in polybrominated diphenyl ethers in indoor and outdoor air from vehicle dismantler factories in southern Taiwan*. Aerosol and Air Quality Research, 2016. **16**(8): p. 1931-1941.
32. Chakraborty, P., et al., *Passive air sampling of polybrominated diphenyl ethers in New Delhi, Kolkata, Mumbai and Chennai: levels, homologous profiling and source apportionment*. Environmental Pollution, 2017. **231**: p. 1181-1187.
33. Yadav, I.C., et al., *Occurrence and source apportionment of halogenated flame retardants in the indoor air of Nepalese cities: implication on human health*. Atmospheric Environment, 2017. **161**: p. 122-131.
34. Shi, T., et al., *Occurrence of brominated flame retardants other than polybrominated diphenyl ethers in environmental and biota samples from southern China*. Chemosphere, 2009. **74**(7): p. 910-916.
35. Kierkegaard, A., J. Björklund, and U. Fridén, *Identification of the flame retardant decabromodiphenyl ethane in the environment*. Environmental Science & Technology, 2004. **38**(12): p. 3247-3253.
36. Newton, S., U. Sellström, and C.A. de Wit, *Emerging Flame Retardants, PBDEs, and HBCDDs in Indoor and Outdoor Media in Stockholm, Sweden*. Environmental science & technology, 2015. **49**(5): p. 2912-2920.
37. Liu, L.-Y., et al., *Trends in the levels of halogenated flame retardants in the Great Lakes atmosphere over the period 2005–2013*. Environment international, 2016. **92**: p. 442-449.
38. Venier, M., Y. Ma, and R.A. Hites, *Bromobenzene flame retardants in the Great Lakes atmosphere*. Environmental science & technology, 2012. **46**(16): p. 8653-8660.
39. Möller, A., et al., *Organophosphorus flame retardants and plasticizers in the atmosphere of the North Sea*. Environmental Pollution, 2011. **159**: p. 3660–3665.
40. Möller, A., et al., *Organophosphorus flame retardants and plasticizers in airborne particles over the Northern Pacific and Indian Ocean toward the polar regions: Evidence for global occurrence*. Environmental Science and Technology, 2012. **46**: p. 3127–3134.
41. Yuxiang, O., *Developments of organic phosphorus flame retardant industry in China [J]*. Chemical Industry and Engineering Progress, 2011. **1**: p. 033.
42. Ohura, T., et al., *Organic air pollutants inside and outside residences in Shimizu, Japan: levels, sources and risks*. Science of the Total Environment, 2006. **366**(2): p. 485-499.
43. Green, N., et al., *Screening of selected metals and new organic contaminants 2007*. Phosphorous flame retardants, polyfluorinated organic compounds, nitro-PAHs, silver, platinum and sucralose in air, wastewater, treatment facilities, and freshwater and marine recipients. Report TA, 2008. **2367**: p. 2008.
44. Marklund, A., B. Andersson, and P. Haglund, *Traffic as a source of organophosphorus flame retardants and plasticizers in snow*. Environmental science & technology, 2005. **39**(10): p. 3555-3562.
45. Möller, A., et al., *Organophosphorus flame retardants and plasticizers in the atmosphere of the North Sea*. Environmental Pollution, 2011. **159**(12): p. 3660-3665.

- 476 46. Salamova, A., et al., *High levels of organophosphate flame retardants in the Great Lakes*
477 *atmosphere*. Environmental Science & Technology Letters, 2013. **1**(1): p. 8-14.
- 478 47. Betts, K., *Flame retardants are the suspected source of a new compound in the environment*.
479 Environmental science & technology, 2009. **44**(2): p. 546-547.
- 480 48. Li, H., et al., *Airborne polybrominated diphenyl ethers (PBDEs), polybrominated dibenzo-p-*
481 *dioxins/furans (PBDD/Fs), and dechlorane plus (DP) in concentrated vehicle parking areas*.
482 Environmental Science and Pollution Research, 2016: p. 1-12.
- 483 49. Hoh, E., L. Zhu, and R.A. Hites, *Dechlorane Plus, a chlorinated flame retardant, in the Great Lakes*.
484 Environmental science & technology, 2006. **40**(4): p. 1184-1189.
- 485 50. Wang, D.-G., et al., *An Asia-specific source of dechlorane plus: concentration, isomer profiles, and*
486 *other related compounds*. Environmental science & technology, 2010. **44**(17): p. 6608-6613.
- 487 51. Ren, N., et al., *Levels and isomer profiles of Dechlorane Plus in Chinese air*. Environmental science
488 & technology, 2008. **42**(17): p. 6476-6480.
- 489 52. Möller, A., et al., *Polybrominated diphenyl ethers vs alternate brominated flame retardants and*
490 *dechloranes from East Asia to the Arctic*. Environmental science & technology, 2011. **45**(16): p.
491 6793-6799.
- 492 53. Salamova, A. and R.A. Hites, *Discontinued and alternative brominated flame retardants in the*
493 *atmosphere and precipitation from the Great Lakes basin*. Environmental science & technology,
494 2011. **45**(20): p. 8698-8706.
- 495 54. Vorkamp, K., et al., *Novel brominated flame retardants and dechlorane plus in Greenland air and*
496 *biota*. Environmental Pollution, 2015. **196**: p. 284-291.
- 497 55. Sverko, E., et al., *Dechlorane Plus and related compounds in the environment: a review*.
498 Environmental science & technology, 2011. **45**(12): p. 5088-5098.
- 499 56. Zehra, A., et al., *Environmental monitoring of organo-halogenated contaminants (OHCs) in surface*
500 *soils from Pakistan*. Science of The Total Environment, 2015. **506**: p. 344-352.
- 501 57. Degrendele, C., et al., *Are atmospheric PBDE levels declining in central Europe? Examination of the*
502 *seasonal and semi-long-term variations, gas-particle partitioning and implications for long-range*
503 *atmospheric transport*. Atmospheric Chemistry and Physics, 2018. **18**(17): p. 12877-12890.
- 504 58. Khan, M.U., et al., *New insight into the levels, distribution and health risk diagnosis of indoor and*
505 *outdoor dust-bound FRs in colder, rural and industrial zones of Pakistan*. Environmental Pollution,
506 2016.
- 507 59. Wei, G.-L., et al., *Organophosphorus flame retardants and plasticizers: Sources, occurrence,*
508 *toxicity and human exposure*. Environmental Pollution, 2015. **196**: p. 29-46.
- 509 60. MacLeod, M., et al., *The origin and significance of short-term variability of semivolatile*
510 *contaminants in air*. Environmental science & technology, 2007. **41**(9): p. 3249-3253.
- 511 61. Liu, Y., et al., *Heterogeneous OH initiated oxidation: a possible explanation for the persistence of*
512 *organophosphate flame retardants in air*. Environmental science & technology, 2014. **48**(2): p.
513 1041-1048.
- 514 62. Regnery, J. and W. Püttmann, *Organophosphorus flame retardants and plasticizers in rain and*
515 *snow from middle Germany*. CLEAN-Soil, Air, Water, 2009. **37**(4-5): p. 334-342.
- 516 63. Finizio, A., et al., *Octanol-air partition coefficient as a predictor of partitioning of semi-volatile*
517 *organic chemicals to aerosols*. Atmospheric Environment, 1997. **31**(15): p. 2289-2296.
- 518 64. Harner, T. and T.F. Bidleman, *Octanol- air partition coefficient for describing particle/gas*
519 *partitioning of aromatic compounds in urban air*. Environmental Science & Technology, 1998.
520 **32**(10): p. 1494-1502.
- 521 65. Liagkouridis, I., A.P. Cousins, and I.T. Cousins, *Physical-chemical properties and evaluative fate*
522 *modelling of 'emerging' and 'novel' brominated and organophosphorus flame retardants in the*
523 *indoor and outdoor environment*. Science of The Total Environment, 2015. **524**: p. 416-426.

66. Goss, K.-U. and R.P. Schwarzenbach, *Linear free energy relationships used to evaluate equilibrium partitioning of organic compounds*. Environmental science & technology, 2001. **35**(1): p. 1-9.
67. Li, Y.-F., W.-L. Ma, and M. Yang, *Prediction of gas/particle partitioning of polybrominated diphenyl ethers (PBDEs) in global air: a theoretical study*. Atmospheric Chemistry and Physics, 2015. **15**(4): p. 1669-1681.
68. Li, Y.-F., et al., *Decabrominated diphenyl ethers (BDE-209) in Chinese and global air: levels, gas/particle partitioning, and long-range transport: is long-range transport of BDE-209 really governed by the movement of particles?* Environmental science & technology, 2016. **51**(2): p. 1035-1042.
69. USEPA, *Example exposure scenarios*. National Center for Environmental Assessment. U.S. Environmental Protection Agency Washington, DC. , 2004a.
70. Wayne R. Ott, A.C.S., Lance A. Wallace, *Exposure Analysis*. 2006: CRC Taylor & Francis, Boca Raton, Florida, USA.
71. Guo, J., et al., *Polybrominated diphenyl ethers in indoor air during waste TV recycling process*. Journal of hazardous materials, 2015. **283**: p. 439-446.
72. Fromme, H., et al., *Brominated flame retardants—Exposure and risk assessment for the general population*. International journal of hygiene and environmental health, 2016. **219**(1): p. 1-23.
73. He, W., et al., *Atmospheric PBDEs at rural and urban sites in central China from 2010 to 2013: residual levels, potential sources and human exposure*. 2014. **192**: p. 232-243.

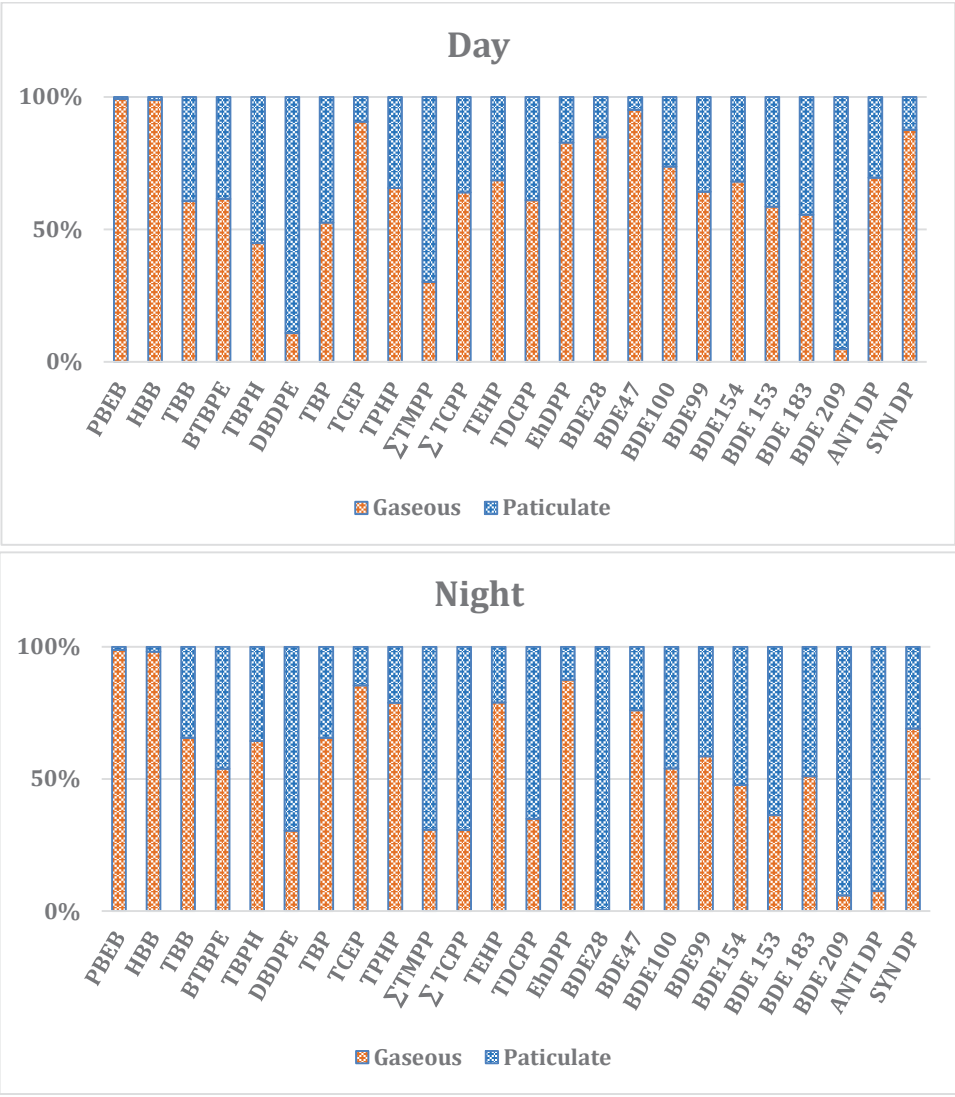


Figure 1: Relative distribution of FRs in gaseous and particulate phase for Day and Night

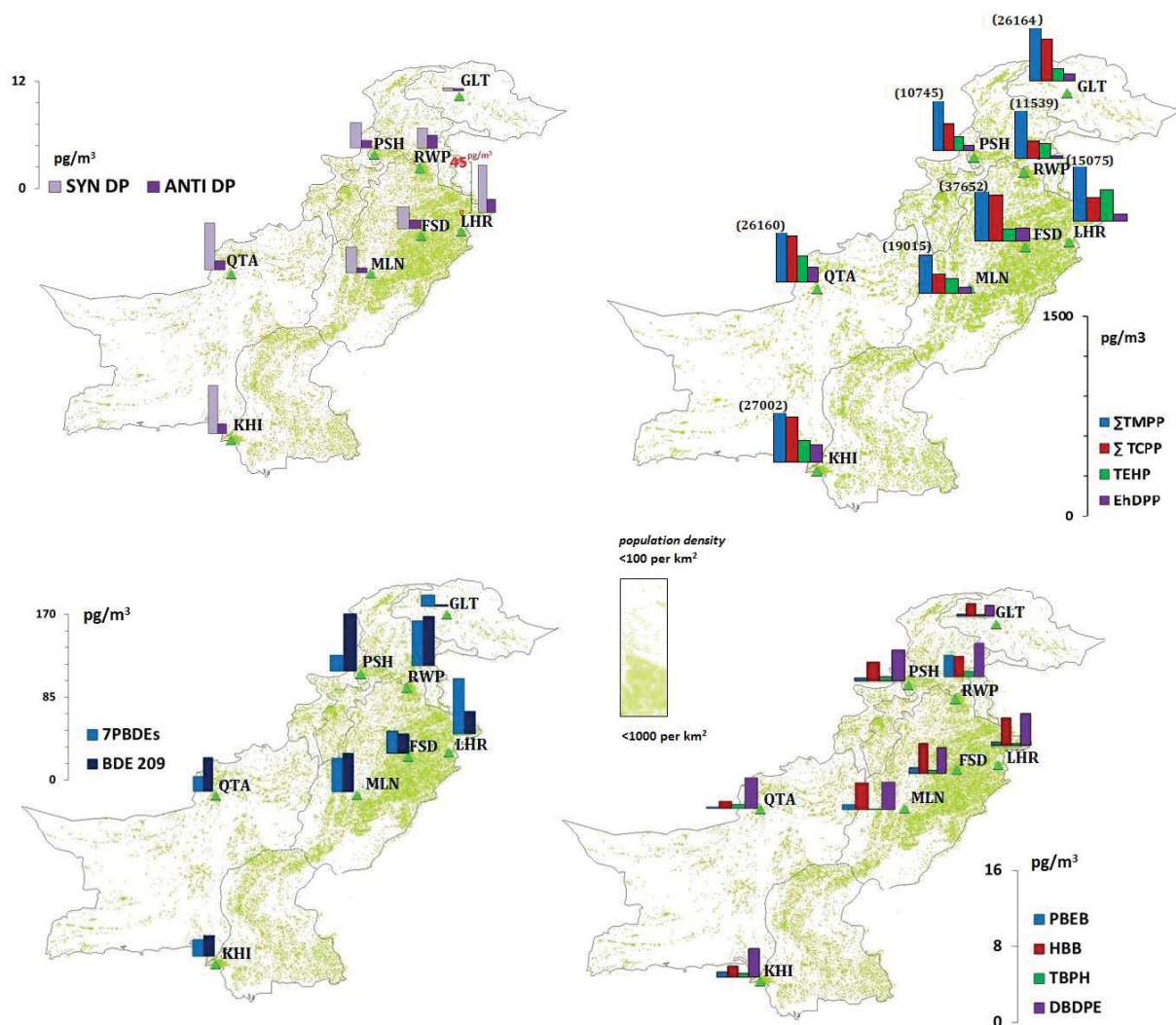
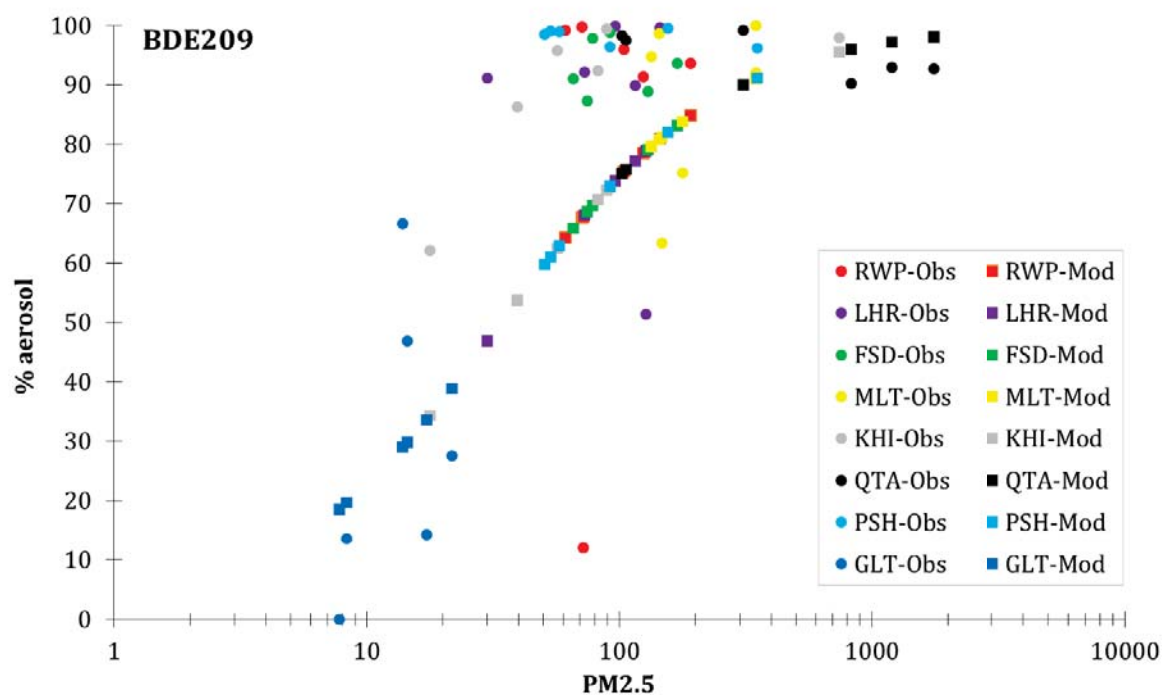


Figure 2: Spatial distribution of FRs in air (gaseous+particulate) in 8 cities of Pakistan. Sum TMPP concentrations are shown in brackets



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