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# Environmental concentration and atmospheric deposition of halogenated flame retardants in soil from Nepal: Source apportionment and soil-air partitioning<sup>☆</sup>

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## ABSTRACT

While various investigations have been driven on polybrominated diphenyl ethers (PBDEs) and other flame retardants (FRs) in different framework around the world, information about contamination and fate of PBDEs and other FRs in developing countries especially in the Indian subcontinent is uncommon. Nepal being located in the Indian subcontinent, very little is known about contamination level of semi-volatile organic pollutants discharged into the environment. This motivated us to investigate the environmental fate of halogenated flame retardant (HFRs) in Nepalese condition. In this study, we investigated the concentration, fate, and sources of 9 PBDEs, 2 dechlorane plus isomers (DPs), and 6 novel brominated flame retardants (NBFRs). Moreover, air-soil exchange and soil-air partitioning were also evaluated to characterize the pattern of air-soil exchange and environmental fate. In general, the concentrations of NBFRs in soil were more prevalent than PBDEs and DPs, and accounted 95% of  $\Sigma$ HFRs. By and large, the concentrations of NBFRs and DPs were measured high in Kathmandu, while PBDEs level exceeded in Pokhara. Principal component analysis (PCA) study suggested contributions from commercial penta-, octa-, and deca-BDEs products and de-bromination of highly brominated PBDEs as the significant source of PBDEs. Likewise, low  $f_{anti}$  ratio suggested DPs in soil might have originated from long-range atmospheric transport from remote areas, while high levels of decabromodiphenyl ethane (DBDPE) in soil were linked with the use of wide varieties of consumer products. The estimated fugacity fraction ( $f$ ) for individual HFR was quite lower ( $<0.05$ ) than equilibrium value, suggesting that deposition and net transport from air to the soil is overwhelming. Soil-air partitioning study revealed neither octanol-air partition coefficient ( $K_{OA}$ ) nor black carbon partition coefficient ( $K_{BC-A}$ ) is an appropriate surrogate for soil organic matter (SOM), subsequently, absorption by SOM has no or little role in the partitioning of HFRs.

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## 1. Introduction

Halogenated flame retardants (HFRs) are semi-volatile organic compounds (SVOCs), which are widely utilized as part of many

domestic and industrial products to counteract fire (WHO, 1997; Tan et al., 2007; Lagalante et al., 2009). Some of their usages in consumer products include electronic casings, synthetic textiles, thermoplastics, foams, synthetic resins and glutinous materials (WHO, 1997; Covaci et al., 2003; Stapleton et al., 2012). Since 1970, PBDEs have been broadly utilized and recognized worldwide as critical contaminants (de Wit et al., 2006; Brits et al., 2016; Yu et al., 2016). PBDEs are likely to adhere to solids (e.g. soil, sediment and particles in the air) and may bio-accumulate after their discharge into the environment (Yun et al., 2008; Cetin, 2014).

Traditionally, PBDEs had been sold in three major commercial formulations known as penta-BDE, octa-BDE and deca-BDE, each of

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which contain a scope of the 209 mono-through deca-brominated congeners (La Guardia et al., 2006). Specific congeners have dominated within the commercial mixtures and are commonly investigated in environmental samples as a marker of the individual compound. More specifically, the tetra-brominated (BDE-47), penta-brominated (BDE-99 and -100), and hexa-brominated (BDE-153 and -154) congeners are representative of penta-BDE formulation, while octa-BDE products are shown by hepta-brominated (BDE-183) and deca-BDE products by the deca-brominated congener (BDE-209). The use of penta- and octa-BDE formulation have been prohibited in many jurisdictions (EU, 2003; NICNAS, 2007; Stapleton et al., 2012) while the most common compounds such as tetra-through hepta-brominated congeners are listed as persistent organic pollutants (POPs) under the United Nations Stockholm Convention 2009 (UNEP, 2009). Recently, considering the recommendation of the Persistent Organic Pollutants Review Committee, the 8th meeting of the Conference of the Parties to the Stockholm Convention held in Geneva, Switzerland during 24 May–5 May 2017 listed commercial deca-BDE too as POPs.

Toxicological reports suggested many adverse impacts on human and animal due to exposure to high concentration of PBDEs ranging from endocrine disruption to neurodevelopmental toxicity (Berghuis et al., 2015; Linares et al., 2015). The widespread environmental occurrence, as well as their dangerous health impact, prompted the worldwide ban on PBDEs and intentional withdrawals in many jurisdictions. The substitution of PBDEs by novel brominated flame retardants (NBFRs) has, be that as may be, displayed a large number of an indistinguishable poisonous attribute from PBDEs and seems to have similar environmental fate. Some of the most widely recognized NBFRs comprise deca-bromodiphenyl ethane (DBDPE), which replaced deca-BDE, bis(2,4,6-tribromophenoxy)ethane (BTBPE) was introduced in place of octa-BDE, and bis(2-ethylhexyl) tetrabromophthalate (TEBP) and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB) are substituents of penta-BDE (Covaci et al., 2011; Ezechias et al., 2014). Hexabromobenzene (HBB), and 2,3,4,5,6-pentabromoethylbenzene (PBEB) are broadly utilized flame retardants supplanting PBDEs in the wide range of polymers (Covaci et al., 2011; Ezechias et al., 2014). Dechlorane Plus (DP) is a chlorinated flame retardant that has been utilized as apart of coating electrical wires and cables, computer connector's fire prevention and numerous manufactured items, for example, nylon or plastic like polypropylene (Hoh et al., 2006; OxyChem, 2007). They are norbornylene derivatives that show flame-retardant and persistent properties similar to PBDEs. Syn- and anti-DP isomers are the significant constituents of technical DPs and have been used in replacement of mirex (Hoh et al., 2006).

Soil composed of organic and inorganic materials is an important environmental matrix for studying fate and behavior of POPs. It assumes an essential part in the dissemination and fate of POPs. Because of wide assimilation capacity of soil, it may serve as a significant supplier and sinks for POPs (Wang et al., 2012; Cetin, 2014). Likewise, it is also a secondary emission source for many SVOCs to groundwater, surface water, and the atmosphere (Tao et al., 2008). Soil quality has been known as a good indicator of environmental contamination and health hazard to human (Meijer et al., 2001). Soil contaminated by PBDEs and NBFRs likewise form potential exposure pathways for humans. While various investigations have been led on PBDEs and other flame retardants in different framework around the world, data, especially on the concentration of PBDEs and other BFRs in developing countries particularly in Indian subcontinent is rare (Eguchi et al., 2013; Zehra et al., 2015; Li et al., 2016a). Such data are extremely pertinent to the worldwide interest for information on the level of SVOCs discharged into the environment. Moreover, information about the

human health impact of HFRs in urban soil is lacking. Although, few past studies revealed serious contamination of brominated- and organophosphate-flame retardant in the air of Nepalese cities (Yadav et al., 2017a,b), very little is known about environmental fate and distribution trends of HFRs in the soil. It was hypothesized that the urban soil in Nepal might also been contaminated with high level of HFRs as they are not regulated in Nepal. This study aims to explore the contamination level, fate, spatial dissemination and sources of HFRs in urban soil of Nepal. Besides, air-soil exchange and soil-air partitioning were assessed to comprehend the influence of soil organic carbon (SOC) and black carbon (BC) in the distribution of HFRs.

## 2. Materials and methods

### 2.1. Soil sampling

About 50 g of surface soil was collected from 4 major cities (i.e. Kathmandu, Pokhara, Birgunj, and Biratnagar) of Nepal during October 2014. Details about study sites and sampling locations are well described in our previous study (Yadav et al., 2017c). Soil samples (vegetation removed) were collected at depth of 0–15 cm using stainless steel shovel designed for the purpose. Details about soil sampling and pretreatment process are discussed elsewhere (Yadav et al., 2016, 2017c). Briefly, a total of 72 surface soil samples were collected and mixed to make 24 representative samples. In this way, each sample was a composite of at least 3 subsamples collected in a different direction at distance of 5 m. After collection, subsamples were properly mixed, wrapped in aluminum foil and packed in a zipper bag. Later, all the soil samples were transported to Organic Geochemistry Laboratory of Guangzhou Institute of Geochemistry, Guangzhou, China where they were stored at -20 °C until analysis.

### 2.2. Determination of TOC and BC

The total organic carbon (TOC) in soil was determined as per method suggested by Ramu et al. (2010). Briefly, about 2–3 g of dried, sieved and homogenized soil was treated with 3 mL of 10% HCl to remove inorganic carbon, washed thrice with Milli-Q water and dried overnight in an oven at 45 °C. A portion of the soil was used to determine TOC. The TOC analysis was performed with Elemental Carbon-Hydrogen-Nitrogen Analyzer (Elementar VARIO EL III). The analysis of BC in soil sample was done following chemothermal oxidation (CTO-375) technique described elsewhere (Gustafsson et al., 2001; Elmquist et al., 2008). In brief, 2–3 g of dried, sieved and homogenized soil was burnt in a muffle furnace to thermal oxidation (375 °C, 18 h) under constant air flow. The soil was then treated with 1 N HCl to remove inorganic carbon. Later, the residual organic carbon in soil was analyzed as BC using Elemental Carbon-Hydrogen-Nitrogen Analyzer (Elementar VARIO EL III).

### 2.3. Extraction and GC-MS analysis

About 10 g of freeze-dried and properly homogenized soil was spiked with 20 ng of PCB 209 as recovery standard and Soxhlet extracted for 24 h with dichloromethane (DCM). The extract was concentrated to a final approximate volume of 2–3 mL by rotary evaporator. The extract was then purified by multilayer silica gel/alumina column followed by anhydrous sodium sulfate. The column was pre-rinsed with 30 mL of hexane and eluted with around 50 mL mixture of DCM/hexane (1:1 vol). The eluent was then concentrated to 0.2 mL under the gentle nitrogen stream. Around 25 µL of iso-octane was added to the GC vial as a solvent keeper.

10 ng of  $^{13}\text{C}$ -PCB141 was added as internal standard before GC-MS analysis.

The chromatographic analysis was done on an Agilent 7890 gas chromatograph coupled to an Agilent 5975C mass selective detector (Mississauga, ON) working in electrochemical negative ionization (ECNI) mode, with HP-5MS column (15 m  $\times$  0.25 mm i. d.  $\times$  0.1  $\mu\text{m}$  film thickness). One  $\mu\text{L}$  of sample was used in splitless mode for GC-MS analysis with an injector temperature of 295  $^{\circ}\text{C}$ . Helium was utilized as a carrier gas with a flow rate of 1.2 mL/min. GC oven temperature was set to an initial temperature of 110  $^{\circ}\text{C}$  for 5 min and raised to 200  $^{\circ}\text{C}$  at a rate of 20  $^{\circ}\text{C}/\text{min}$  (held for 4.5 min); extended at a rate of 10  $^{\circ}\text{C}/\text{min}$  to the last temperature of 310  $^{\circ}\text{C}$  (held for 12 min). The transfer line and ion source temperatures were 280  $^{\circ}\text{C}$  and 230  $^{\circ}\text{C}$ , respectively. Six different compounds of NBFrs (TBPB, PBEB, BTBPE, TBB, HBB, and DBDPE), 9 congeners of PBDEs (BDE-28, BDE-35, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209), 2 congeners of DPs (anti- and syn-isomer) were targeted and quantified. The GC-MS parameters of HFRs analyzed in this study are detailed in our previous study (Yadav et al., 2017a).

#### 2.4. QA/QC

Spiked recovery standard, field blanks ( $n = 3$ ) and laboratory blanks ( $n = 10$ ) were analyzed for HFRs by GC-MS alike soil sample to mark any kind of interference, cross-contamination, and GC-MS detection limit. Target compounds (PBDEs, NBFrs and DPs) were rarely detected or low detected in blank samples. The method detection limit (MDL) was calculated as 3 times standard deviation plus the average of all the blank samples. In case of non-detection of HFRs in the blank, the MDL was 3 times S/N of the least concentration spiked standard. The MDL ranged from 0.19–0.27  $\mu\text{g}/\text{g}$ , 0.18–0.29  $\mu\text{g}/\text{g}$ , and 6.1–13.3  $\mu\text{g}/\text{g}$  for PBDEs, DPs and NBFrs, respectively. The average standard recoveries for PCB 209 in all samples ranged from 92–121% and relative standard deviations were less than 15%. For calculation purpose, the concentrations of PBDEs, DPs and NBFrs were blank corrected but not corrected for recovery. Detailed QA/QC is discussed in Supplementary information.

#### 2.5. Statistical analysis

Statistical analysis of GC-MS quantified data (min, max, median, and standard deviation) and graphical presentation (box and whisker plots, profile and relative abundance) were made with MS excel 2010 and the IBM SPSS statistics (version 21), respectively. Measured data with below detection limit (BDL) concentration were set as zero for computation and analysis purpose. The spatial distribution map of HFRs was drawn utilizing Arc GIS geospatial (version 10.3) software.

#### 2.6. Air-soil exchange

Fugacity fraction ( $ff$ ) is the most popular and widely used approach for characterizing the pattern of air-soil exchange (Mackay, 2001; Cabrerizo et al., 2011; Aliyeva et al., 2012; Devi et al., 2014; Degrendele et al., 2016). It is the ratio of the soil fugacity to the sum of the fugacity in soil and air. Mathematically, it is expressed as:

$$ff = f_s / (f_A + f_s) \quad (1)$$

where,  $f_s$  is soil fugacity, and  $f_A$  denotes air fugacity. The  $f_s$  and  $f_A$  can be additionally computed by following condition (Cabrerizo et al., 2011; Aliyeva et al., 2012; Degrendele et al., 2016).

$$f_s = 1 \times 10^{-9} C_s RT / 0.411 \phi_{OM} K_{OA} MW \quad (2)$$

$$f_A = 1 \times 10^{-9} C_A RT / MW \quad (3)$$

where  $C_A$  represents air concentration ( $\text{ng}/\text{m}^3$ ) while  $C_s$  denotes the soil concentration ( $\text{ng}/\text{g}$ ) of individual HFR. The SOM characterizes the fugacity capacity of soils (Mackay, 2001), whereas fugacity of air is fundamentally distinguished as air concentration. In this study, air fugacity was figured using atmospheric concentration of HFRs acquired from the passive sampling of our previous study (Yadav et al., 2017a). Likewise, soil fugacity was assessed in view of SOM measured in surface soil.  $R$  symbolizes universal gas constant (8.314 Pa  $\text{m}^3/\text{mol}/\text{K}$ ),  $T$  denotes the average absolute temperature ( $\text{K}$ ),  $\phi_{OM}$  is the representative of the soil organic matter (which is 1.5 times of TOC),  $K_{OA}$  characterizes the octanol-air partition coefficient and was acquired from Wania et al. (2002) and Harner and Shoeib (2002), and 0.411 is the relationship coefficient constant between  $K_{SA}$  and  $K_{OA}$ . Hypothetically,  $ff$  value equal to 0.5 shows equilibrium,  $ff$  value greater than 0.5 demonstrates volatilization and net outflow into the air, and  $ff$  value lower than 0.5 indicates accumulation and net transport from the air to soil. Notwithstanding, Harner et al. (2001) proposed  $ff$  value greater than 0.7 for net volatilization considering the uncertainty or potential error in  $ff$ .

#### 2.7. Soil-air partitioning

Soil-air partitioning is a vital diffusive process that significantly influences the fate of organic compounds in the environment, and is defined as the ratio of chemical concentrations in soil to the concentrations in air at equilibrium (Cabrerizo et al., 2009). This is most commonly used approach for predicting the partitioning behavior of organic chemicals between air and soil. In this study, soil-air partitioning coefficient was evaluated based on the individual concentration of HFR in soil and air. The concentrations of HFRs measured in the soil in this study were utilized to estimate the soil-air partitioning coefficient, while air concentrations of HFRs were obtained from our previous study of passive sampling (Yadav et al., 2017a). The soil-air partitioning coefficient  $K_{SA}$  ( $\text{L}/\text{Kg}$ ) can be calculated as (Cabrerizo et al., 2009):

$$K_{SA} = 1 \times 10^9 C_s / C_A \quad (4)$$

where,  $C_s$  denotes the concentration of individual HFR in soil ( $\text{ng}/\text{g}$ ),  $C_A$  represents the concentration in air ( $\text{pg}/\text{m}^3$ ).

Additionally, the TOC and BC-based  $K_{SA}$  were estimated by absorption model proposed by Finizio et al. (1997) and Ribes et al. (2003). This model accepts that absorption into the soil organic matter is the fundamental process accountable for soil-air partitioning. Mathematically, it is expressed as follows:

$$K_{SA} = 1.5 (f_{TOC} / \delta_{OCT}) K_{OA} \quad (5)$$

where  $f_{TOC}$  is the fraction of total organic carbon ( $\text{g}/\text{g}$  dw),  $\delta_{OCT}$  is the octanol density (0.820  $\text{kg}/\text{L}$  at 20  $^{\circ}\text{C}$ ), and  $K_{OA}$  denotes octanol-air partition coefficient. To investigate the role of BC in adsorption of HFRs in soil, the  $K_{BC-A}$  model was used (Ribes et al., 2003), which mathematically can be expressed as:

$$K_{SA} = 1.5 (f_{TOC} / \delta_{OCT}) K_{OA} + f_{BC} K_{BC-A} \quad (6)$$

where,  $f_{BC}$  denotes the fraction of BC ( $\text{g}/\text{g}$  dw) in the soil, while  $K_{BC-A}$  signifies the black carbon air partition coefficient.  $K_{BC-A}$  can further be estimated as follows (Ribes et al., 2003):

$$\text{Log } K_{BC-A} = -0.85 \text{Log } P_L + 8.94 - \text{Log } (998/A_{EC}) \quad (7)$$

$A_{EC}$  represents the specific surface area of BC which is  $100 \text{ m}^2/\text{g}$  (Dachs et al., 2004; Prevedouros et al., 2008).

The  $K_{OA}$  and  $K_{BC-A}$  for HFR congeners were acquired from literature and are presented in Table S1.

### 3. Results and discussion

#### 3.1. Overall comments on concentration of HFRs

The concentrations of  $\sum$ HFRs (sum of PBDEs, DPs and NBFRs) measured in the soil in this study have been summarized in Table S2. Overall, the concentration of  $\sum$ HFRs in the soil in this study ranged from 9.50–3320 ng/g dw (median 144 ng/g dw). The NBFRs were measured most abundant FRs followed by DPs and PBDEs, and accounted for 95%, 3% and 2% of  $\sum$ HFRs, respectively. The concentration of  $\sum$ NBFRs,  $\sum$ DPs and  $\sum$ PBDEs in soil ranged from 8.89–3030 ng/g dw (median 137 ng/g dw), 0.16–174 ng/g dw (median 3.84 ng/g dw), and 0.45–114 ng/g dw (median 3.56 ng/g dw), respectively. Among the different group of HFRs, the concentration of DBDPE was measured extremely high in the soil. The concentration of DBDPE in soil ranged from 8.78–2970 ng/g dw (median 135 ng/g dw), and accounted for 94% of  $\sum$ HFRs. The level of DPDBE was measured very high among different NBFRs, and accounted for 99% of  $\sum$ NBFRs.

#### 3.2. Polybrominated diphenyl ethers (PBDEs)

Results of  $\sum$ PBDEs,  $\sum$ DPs, and  $\sum$ NBFRs together with their individual congener measured in the soil from Nepalese cities have been illustrated in Table 1. PBDE was detected in all the soil samples with 100% detection frequency (DF). The highest level of  $\sum$ PBDEs was measured in Pokhara, while least concentration detected in Biratnagar (Fig. 1). The concentration of  $\sum$ PBDEs ranged from 1.58–49.7 ng/g dw (median 10.1 ng/g dw), 1.4–103 ng/g dw (median 6.2 ng/g dw), 0.94–32.2 ng/g (median 4.05 ng/g dw) and 0.87–17.8 ng/g dw (median 2.70 ng/g dw) in Pokhara, Kathmandu, Biratnagar and Birgunj, respectively. The level of  $\sum$ PBDEs measured in the soil in this study was compared with similar previous studies around the world and are presented in Table S3. The level of  $\sum$ PBDEs in soil in this study was 5–10 times higher than those reported in soil from South Korea (0.65–9.3 ng/g) (Li et al., 2016a), Vietnam (0.2–2.4 ng/g) (Li et al., 2016a), India (0.13–13 ng/g) (Li et al., 2016a), and Pakistan (0.04–2.4 ng/g) (Ali et al., 2015). However, the  $\sum$ PBDEs level observed in soil in this study was much lower than those reported in soil from Shanghai China (6–39 ng/g) (Wu et al., 2015), West midland UK (2.3–49 ng/g) (Drage et al., 2016), and Kocaeli Turkey (0.7–203 ng/g) (Cetin, 2014). Moreover, 7–10 folds greater concentration of  $\sum$ PBDEs than this study was previously reported in the urban soil in Japan (32–740 ng/g) (Li et al., 2016a) and China (5.13–1160 ng/g) (Hong et al., 2016).

In this study, the concentration of  $\sum$ PBDEs was mostly dominated by BDE-209 and ranged from 0.42–43.2 ng/g dw, 0.67–38.4 ng/g dw, 0.73–9.10 ng/g dw, and 0.34–9.45 ng/g dw in Kathmandu, Pokhara, Birgunj, and Biratnagar, respectively (Fig. 1). Significantly high level of BDE-209 in soil in this study suggests their concurrence in soil with the commercial deca-BDE formulation, indicating local use in consumer items (BSEF, 2013). This finding of BDE-209 in the soil in this study is consistent with the previous study by McGrath et al. (2017), who also discovered high level of BDE-209 in the urban soil in Australia. Next to BDE-209, BDE-99 was the second most abundant brominated compound measured in soil, and ranged from 0.49–1.32 ng/g dw. BDE-99 is the significant constituents (49%) of commercial penta-BDE (La Guardia et al., 2006). Moreover, slightly high level of BDE-99 (low

brominated congener) in soil can also results from debromination of highly brominated PBDEs (such as BDE-209) under different temperature and pressure (Ma et al., 2009). Nepal being warm region, high air temperature can also cause high emission of PBDEs from household products (Yu et al., 2012). The BDE-153 and BDE-183 were other abundant congeners detected in soil after BDE-209 and BDE-99, and were in the range of, 0.34–0.93 ng/g dw, and 0.18–0.63 ng/g dw, respectively. BDE-153 and -183 represent octa-BDEs and result from handling of e-waste materials (Cahill et al., 2007; Parajuly et al., 2017). Among three commercial PBDE formulations, deca-BDEs was identified as most abundant, followed by octa-BDEs, and penta-BDEs, and accounted for 45%, 29% and 26% of  $\sum$ PBDEs, respectively (Fig. S1).

The profiles of individual PBDE are shown in Fig. 2 and Fig. S2. It is evident from Fig. 2 that BDE-209 was most abundant congener in soil the in all sites. Individually, BDE-209 was measured highest among PBDEs, and accounted for 39–64% of  $\sum$ PBDEs. Next to BDE-209, BDE-99 and BDE-153 were also measured high in soil, and accounted for 12–18% and 9–18% of  $\sum$ PBDEs, respectively. This pattern of PBDEs suggests usage of commercial BDE products (penta-BDE, octa-BDE and deca-BDE), although none of these commercial BDEs have been produced in Nepal. Previously, high levels of BDE-47, -99 and -183 in soil at e-waste recycling sites have been reported to link with past use of commercial BDEs in electronic goods (Tang et al., 2014).

The spatial distribution map of PBDEs from four Nepalese cities has been shown in Fig. 3. It is obvious from Fig. 3 that extremely high levels of  $\sum$ PBDEs were observed at KTS 4 (88.7 ng/g dw) and KTS5 (49.8 ng/g dw) in Kathmandu, PKS 3 (46.1 ng/g dw) in Pokhara, and BTS 5 (30.8 ng/g dw) in Biratnagar. Higher concentrations of  $\sum$ PBDEs were also prevalent at PKS 5 (19.3 ng/g dw) and PKS 6 (19.3 ng/g dw) in Pokhara, and BRS 3 (17.3 ng/g dw) in Birgunj. The lowest concentrations of  $\sum$ PBDEs were detected at BRS 2 (0.93 ng/g dw) and BRS 6 (0.94 ng/g dw) in Birgunj. This finding suggests that high levels of PBDEs in soil are related to close proximity to the residential/commercial area together with intense traffic zone and industrial areas.

#### 3.3. Dechlorane plus (DPs)

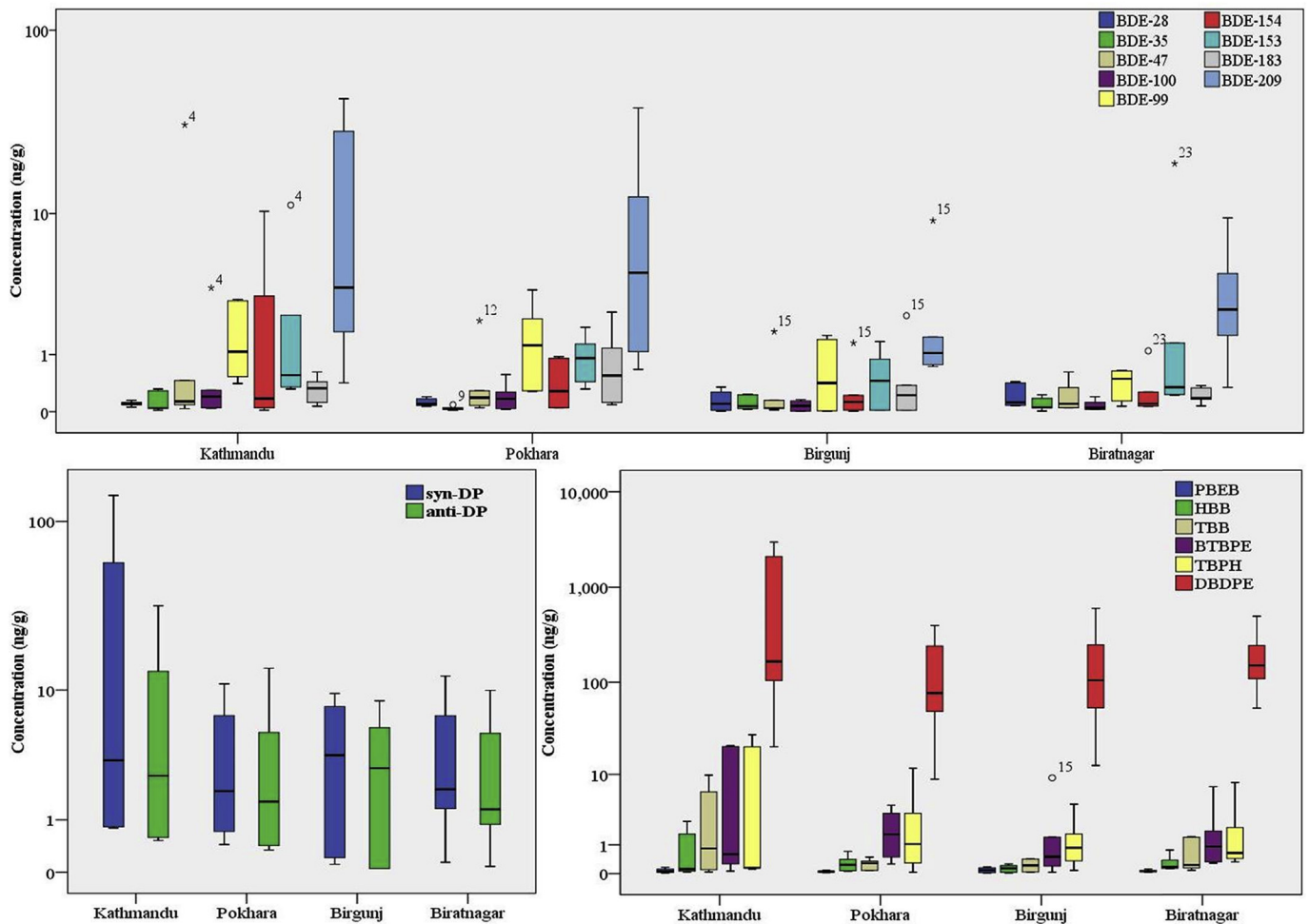
The concentrations of  $\sum$ DPs together with individual congeners are shown in Fig. 2 and summarized in Table 1. The concentration of  $\sum$ DPs measured in soil in this study ranged from 1.31–174 ng/g dw (median 7.82 ng/g dw), 0.78–24.6 ng/g dw (median 4.23 ng/g dw), 0.16–18.1 ng/g dw (median 7.97 ng/g dw), and 0.22–22.2 ng/g dw (median 3.42 ng/g dw) in Kathmandu, Pokhara, Birgunj, and Biratnagar, respectively. In general, syn-DP was more dominant in soil than the anti-DP, and accounted for 56% of  $\sum$ DPs. The level of  $\sum$ DPs in Kathmandu (median 7.82 ng/g dw) and Birgunj (median 7.97 ng/g dw) was two folds greater than those in Pokhara (median 4.23 ng/g) and Biratnagar (median 3.42 ng/g dw). The concentrations of  $\sum$ DPs measured in soil in this study were consistent with previously reported in urban soil from Stockholm Sweden (0.4–14 ng/g) (Newton et al., 2015), North China (nd–12 ng/g) (Ma et al., 2009), and Pakistan (0.17–2.6 ng/g) (Ali et al., 2015) (Table S4). The concentration of  $\sum$ DPs in Kathmandu was 2–3 times higher than those reported at e-waste recycling facility and open burning sites in Vietnam (Someya et al., 2016), and rural soil in China (0.82–52 ng/g) (Wang et al., 2010), but was comparable to DPs level reported in urban soil in China (1.2–156 ng/g) (Hong et al., 2016). As depicted in Fig. 3, the spatial distribution map of DPs indicated less variation in concentration of  $\sum$ DPs with respect to space. However, extremely high levels of  $\sum$ DPs were observed at KTS 4 (174 ng/g dw) and KTS 5 (71 ng/g dw) in Kathmandu.

The ratio of the concentration of anti-DP to the concentration of



**Table 1**  
Descriptive statistics of PBDEs, DPs and NBFRs in soil (ng/g) from Nepal.

Compounds	Kathmandu				Pokhara				Birgunj				Biratnagar			
	Min	Max	Median	SD	Min	Max	Median	SD	Min	Max	Median	SD	Min	Max	Median	SD
BDE-28	0.06	0.15	0.10	0.03	0.07	0.20	0.10	0.05	0.01	0.35	0.11	0.14	0.08	0.44	0.12	0.17
BDE-35	0.02	0.32	0.05	0.14	0.02	0.09	0.05	0.02	0.03	0.24	0.07	0.09	0.01	0.23	0.06	0.09
BDE-47	0.04	31.1	0.14	12.6	0.05	2.01	0.19	0.76	0.02	1.64	0.05	0.65	0.05	0.62	0.11	0.23
BDE-100	0.04	3.48	0.21	1.36	0.03	0.57	0.17	0.20	0.01	0.16	0.08	0.07	0.03	0.20	0.05	0.07
BDE-99	0.41	2.89	1.13	1.15	0.28	3.37	1.32	1.23	0.01	1.52	0.49	0.72	0.07	0.65	0.50	0.26
BDE-154	0.02	10.3	0.18	4.09	0.05	0.95	0.31	0.43	0.01	1.30	0.13	0.50	0.07	1.09	0.11	0.40
BDE-153	0.32	11.2	0.56	4.30	0.32	1.78	0.93	0.55	0.02	1.34	0.50	0.56	0.22	19.1	0.34	7.63
BDE-183	0.07	0.62	0.33	0.20	0.09	2.34	0.63	0.90	0.02	2.20	0.23	0.84	0.07	0.37	0.18	0.11
BDE-209	0.42	43.2	3.51	18.0	0.67	38.4	6.37	14.5	0.73	9.10	1.06	3.32	0.34	9.45	2.60	3.28
Penta-BDEs	0.55	37.7	1.57	15.2	0.43	6.15	1.78	2.24	0.05	3.67	0.72	1.58	0.23	1.91	0.77	0.73
∑PBDEs	1.40	103	6.19	41.9	1.58	49.7	10.1	18.7	0.87	17.8	2.70	6.89	0.94	32.2	4.05	12.2
syn-DP	0.79	141	4.57	56.6	0.44	10.9	2.33	4.25	0.11	9.51	4.65	4.33	0.14	12.2	2.08	4.61
anti-DP	0.52	32.4	3.25	12.5	0.34	13.7	1.90	5.17	0.05	8.54	3.32	3.47	0.08	9.96	1.34	3.80
∑DPs	1.31	174	7.82	69.1	0.78	24.6	4.23	9.43	0.16	18.1	7.97	7.81	0.22	22.2	3.42	8.41
f <sub>anti</sub>	0.40	0.19	0.42	0.18	0.44	0.56	0.45	0.55	0.31	0.47	0.42	0.44	0.36	0.45	0.39	0.45
PBEB	0.01	0.16	0.05	0.06	0.02	0.08	0.05	0.02	0.01	0.17	0.09	0.07	0.03	0.11	0.06	0.03
HBB	0.04	2.54	0.12	1.07	0.05	0.71	0.24	0.26	0.01	0.26	0.14	0.10	0.12	0.76	0.17	0.25
TBB	0.04	9.82	1.08	4.08	0.07	0.49	0.29	0.16	0.03	0.44	0.22	0.18	0.08	1.43	0.23	0.64
BTBPE	0.06	21.1	0.61	10.6	0.26	4.23	1.91	1.77	0.03	9.13	0.50	3.54	0.28	7.14	0.98	2.64
TBPH	0.11	27.7	0.15	12.6	0.03	11.8	1.04	4.48	0.08	4.37	0.87	1.57	0.32	8.00	0.64	3.00
DBDPE	20.4	2970	167	1280	8.78	395	81.4	148	12.7	603	107	218	52.58	493	150	157
∑NBFR	20.7	3030	169	1310	9.21	412	84.9	154	12.8	617	109	224	53.41	511	153	163
<b>∑HFRs</b>	<b>23.4</b>	<b>3310</b>	<b>183</b>	<b>1420</b>	<b>11.6</b>	<b>487</b>	<b>99.2</b>	<b>182</b>	<b>13.9</b>	<b>653</b>	<b>119</b>	<b>239</b>	<b>54.6</b>	<b>565</b>	<b>160</b>	<b>184</b>



**Fig. 1.** Box and whisker-plots showing lower and upper concentrations of PBDEs, DPs and NBFRs in soil (ng/g). The central box represents the concentration from 25 to 75 percentile. The middle bold line represents the median value. The asterisk/stars are an extreme outliers that are >3-times beyond interquartile range.

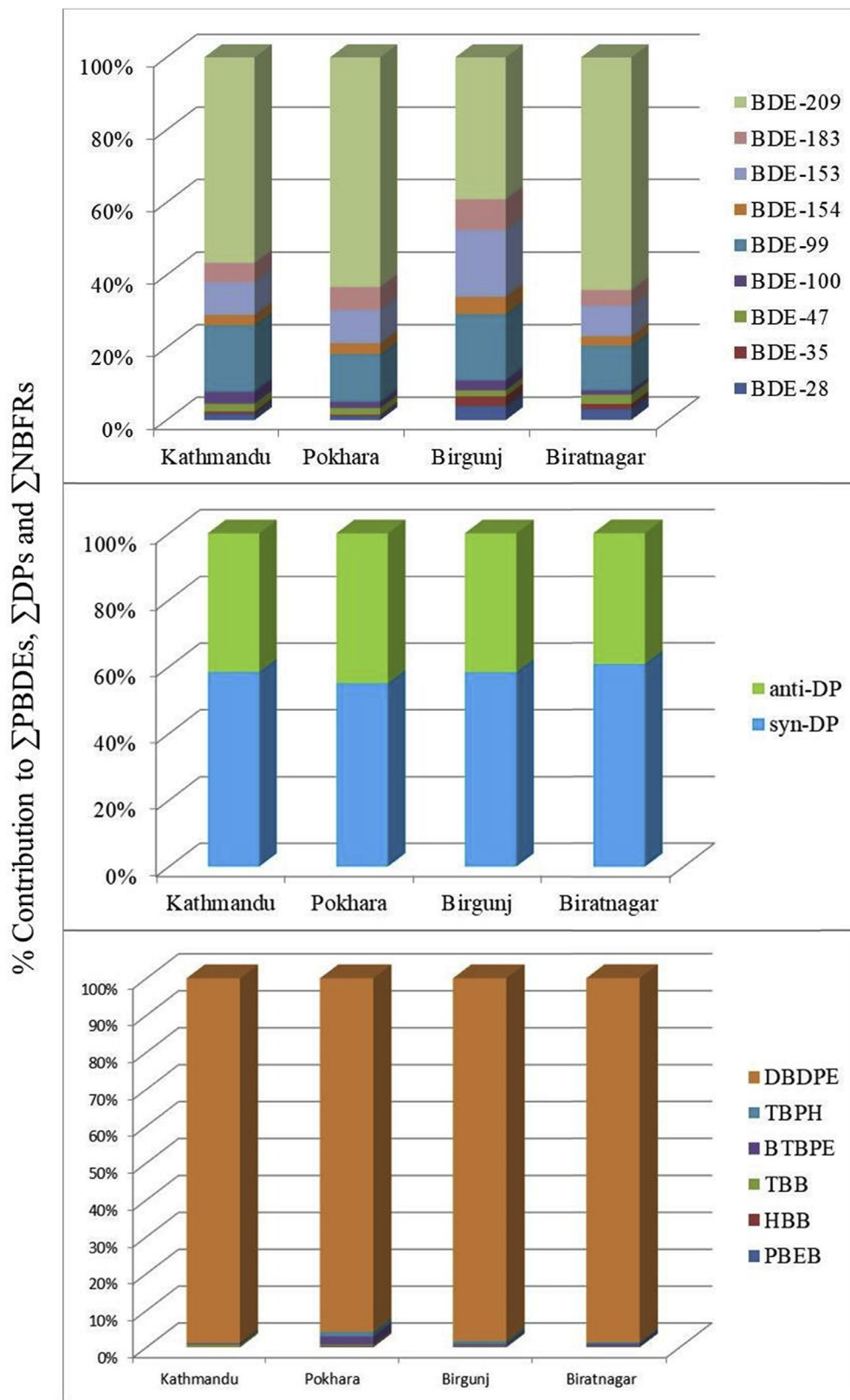


Fig. 2. Profile of Individual HFR showing % contribution to  $\Sigma$ PBDEs,  $\Sigma$ DPs and  $\Sigma$ NBFs.

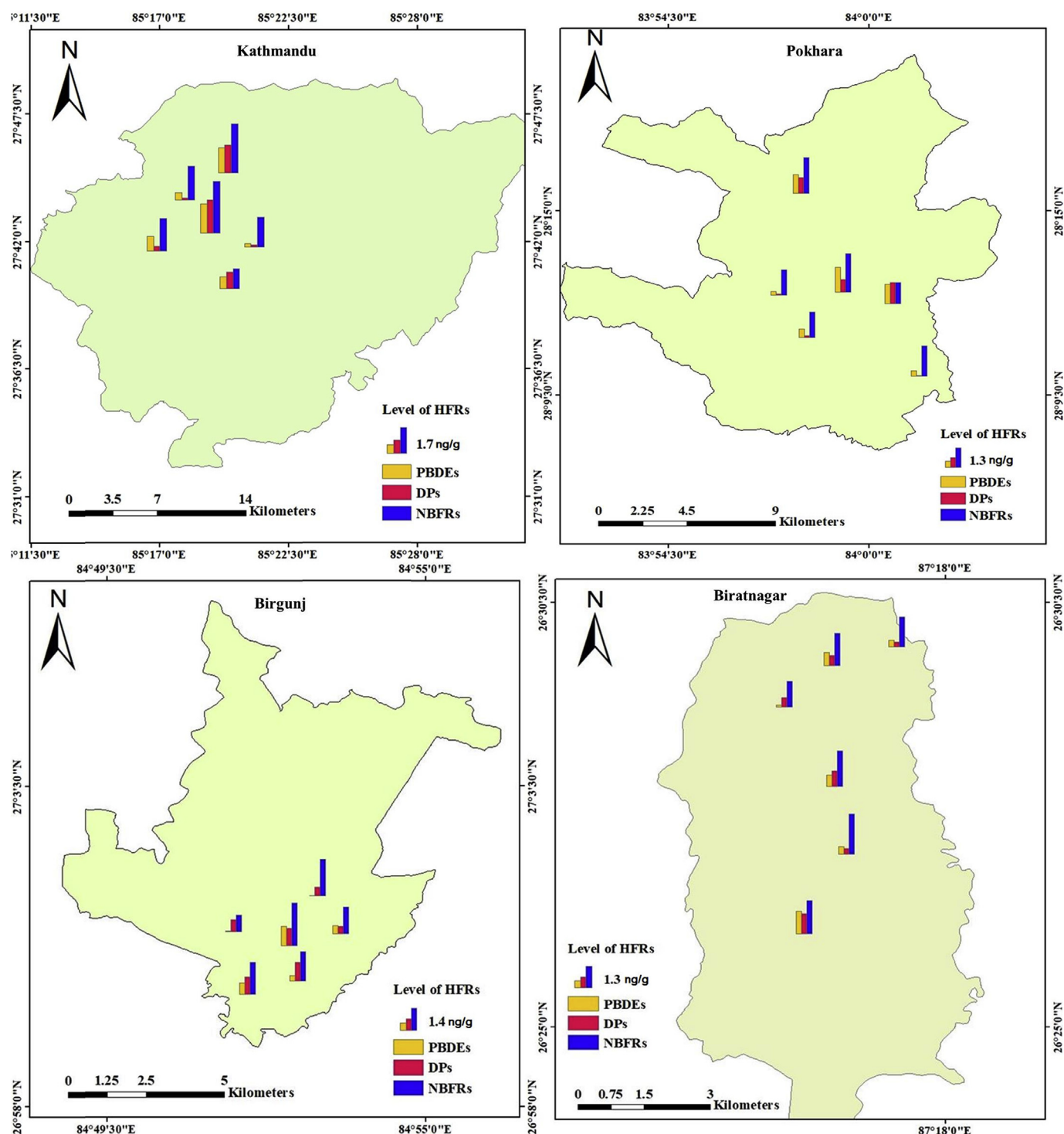


Fig. 3. Map of the Nepalese cities showing spatial distribution of  $\Sigma$ PBDEs,  $\Sigma$ DPs, and  $\Sigma$ NBFrs in soil (ng/g).

$\Sigma$ DPs ( $f_{\text{anti}}$  ratio) is widely used and accepted approach for studying the transport and fate of two structural isomers of DPs (Hoh et al., 2006; Qiu et al., 2007). The  $f_{\text{anti}}$  ratio close to 0.75 is an indication of technical DP (Qiu et al., 2007). The estimated  $f_{\text{anti}}$  ratio in soil in this study is quite lower than the ratio of technical DP. The estimated  $f_{\text{anti}}$  ratio in soil in this study ranged from 0.19–0.40 (median 0.42), 0.44–0.56 (median 0.45), 0.31–0.47 (median 0.42), and 0.36–0.45 (median 0.39), in Kathmandu, Pokhara, Birgunj and

Biratnagar, respectively. The estimated  $f_{\text{anti}}$  ratio in this study was about 1–2 folds lower than US commercial products (0.70) and Chinese products (0.60) (Hoh et al., 2006; Wu et al., 2010). Slightly low  $f_{\text{anti}}$  ratio calculated in this study is indicative of low influence of technical DP contamination. With respect to atmospheric degradation and isomerization of anti-DP over syn-DP, it is believed that high level of DPs might be impacted by long-range atmospheric transport from remote DP source (Yadav et al., 2017a).

### 3.4. Novel brominated flame retardants (NBFRs)

Results of NBFRs concentrations measured in the soil are summarized in Table 1. All the six NBFR congeners were detected in soil with 100% DF. Significantly high levels of  $\sum$ NBFRs were measured in Kathmandu, followed by Biratnagar, Birgunj, and Pokhara, and ranged 23.4–3310 ng/g (median 183 ng/g dw), 11.6–487 ng/g dw (median 160 ng/g dw), 13.9–653 ng/g dw (median 119 ng/g dw), and 54.6–565 ng/g dw (median 99.2 ng/g dw), respectively (Fig. 1). The levels of  $\sum$ NBFRs measured in the soil in this study were compared with past studies around the world (Table S5). The concentration of  $\sum$ NBFRs in soil in this study was consistent with the level of  $\sum$ NBFRs reported in manufacturing sites in China (12–344 ng/g) (Zhu et al., 2014), manufacturing and waste disposal sites in Australia (nd–385 ng/g and 0.34–320 ng/g) (McGrath et al., 2017). The level of  $\sum$ NBFRs detected in this study was greater than those reported in urban soil in Indonesia (0.07–80.3 ng/g) (Ilyas et al., 2011) and Sweden (0.06–0.22 ng/g) (Newton et al., 2015), but much lower than that reported at manufacturing sites in China (5.4–9200 ng/g) (Li et al., 2016b).

DBDPE was identified as the most dominant congener (81–167 ng/g dw) in soil among different NBFRs, and accounted for 99% of  $\sum$ NBFRs (Fig. 2 and S2). It is one of the most utilized NBFR in consumer items (as plastics, polyester, nitrile, rubber, textiles and adhesive) (WHO, 1997; EFSA, 2012). The DBDPE level measured in soil was about 30 times higher than BDE-209. BDE-209 is the significant component of deca-BDE. The occurrence of an extremely high level of DBDPE than BDE-209 in soil indicates its application in replacement of deca-BDE. This finding is in good agreement with the previous study by McGrath et al. (2017) who also reported the high level of DBDPE in the urban soil in Melbourne, Australia. Other NBFR congeners in the soil follows the order TBPH > BTBPE > TBB > HBB and PBEB.

TBPH and TBB are the two major components in Firemaster 550 (FM550) and have been utilized in substitution to PBDEs (Stapleton et al., 2008). The concentration of TBPH in soil in this study ranged from 0.11–27.7 ng/g dw (median 0.15 ng/g dw), 0.03–11.8 ng/g dw (median 1.04 ng/g dw), 0.08–4.37 ng/g dw (median 0.87 ng/g dw), 0.32–8.0 ng/g dw (0.64 ng/g dw) in Kathmandu, Pokhara, Birgunj and Biratnagar, respectively. The concentration of TBB was lower in soil and ranged from 0.04–9.82 ng/g dw, 0.07–0.49 ng/g dw, 0.03–0.44 ng/g dw and 0.08–1.43 ng/g dw, in Kathmandu, Pokhara, Birgunj, and Biratnagar, respectively.

BTBPE is highly utilized in polystyrene, thermoset resin, acrylonitrile butadiene styrene, thermoplastics, coatings and polycarbonate (WHO, 1997). In this study, the concentration of BTBPE ranged from 0.06–21.1 ng/g dw, (median 0.61 ng/g dw), 0.26–4.23 ng/g dw (median 1.91 ng/g dw), 0.03–9.13 ng/g dw (median 0.50 ng/g dw), and 0.28–7.14 ng/g dw (median 0.98 ng/g dw), in Kathmandu, Pokhara, Birgunj and Biratnagar, respectively. The level of BTBPE measured in soil was comparable with those reported in Qingyuan Southern China (0.06–6.19 ng/g) (Shi et al., 2009), and e-waste recycling sites in Northern China (0.25–5.90 ng/g) (Hong et al., 2016).

The spatial distribution maps of  $\sum$ NBFRs are shown in Fig. 3. It is evident from Fig. 3 that the high levels of  $\sum$ NBFRs were measured at KTS 4 and KTS 5 in Kathmandu. The elevated levels of  $\sum$ NBFRs were also prevalent at BRS 3 in Birgunj and BTS 6 in Biratnagar. The lowest concentration of  $\sum$ NBFRs was observed at BRS 2 and PKS 6 in Birgunj and Pokhara, respectively.

### 3.5. Principal component analysis (PCA)

To evaluate the possible sources of HFRs in Nepalese soil, a multivariate principal component analysis (PCA) was applied to the

whole dataset of HFRs. Four major principal components (PC) were extracted with Eigenvalue greater than 1, and accounted for 83.6% of total variance. The factor loading of HFRs dataset following varimax orthogonal rotation are presented in Table 2 and Fig. S3. Factor loadings are the better interpreter of the relationship between sources composition and corresponding individual component. PC 1, contained 55.09% of the total variance and was characterized by the strong grouping of PBDEs (except BDE-28 and -183), DPs and NBFRs (except PBEB). This indicates common sources of HFRs resulting from open burnings, combustion of electronic materials and e-waste recycling activities (Parajuly et al., 2017). BDE-209 is an indicator of contribution from commercial deca-BDE formulations (Zhang et al., 2014; Wu et al., 2015). Consequently, BDE-209 also results from use of consumer items such as electrical and electronic items, textiles, plastics, polystyrene, polybutylene terephthalate, and polyamides (Wu et al., 2015). Likewise, penta-BDEs and octa-BDEs are major commercial products of PBDEs infused in many obsolete consumer materials. Significantly high loadings on low mass PBDEs are the indication of de-bromination of highly brominated PBDEs in presence of extreme light (Kajiwara et al., 2008; Shih et al., 2012; Tue et al., 2016). Nepal being a tropical and warm region, it receives more sunshine; hence, sufficient light irradiation and pressure differences can significantly stimulate the de-bromination process (Harrad and Abdallah, 2011). Hence, PC 1 is referred as combined source contribution from penta-, octa-, and deca-BDE formulations together with de-bromination of highly brominated PBDEs. PC 2 accounted for 13.2% of total variance, and was highly loaded with BDE-99 (0.575), BDE -183 (0.562), BDE-28 (0.616) and PBEB (0.574). PC 2 was also significantly loaded with TOC (0.608) and BC (0.646). BDE-28 and -99 are the major components of penta-BDE. BDE-183 is indicative of commercial octa-BDE. Octa-BDE was mainly used in thermosetting plastic and polycarbonate. Hence, PC 2 can be considered as source contribution from commercial penta- and octa-BDEs. PC 3 explained 8.55% of total variance and was highly loaded with BDE-28 (0.707) and BDE-35(0.520). BDE-35 is rarely detected in the environment, while BDE-28 is the constituent of penta- and octa-BDEs, and part of them is associated with degradation of BDE-209 (La Guardia et al., 2006; Tokarz et al., 2008). Hence, PC3 represents combined source from penta- and octa-BDEs and degradation of BDE-209. PC 4 contained

**Table 2**

Principal component analysis of individual HFR after varimax rotation. Factor loadings greater than 0.50 are in bold.

Compounds	PC 1	PC 2	PC 3	PC 4
BDE-28	0.121	<b>0.616</b>	<b>0.707</b>	0.109
BDE-35	<b>0.729</b>	0.222	<b>0.520</b>	-0.206
BDE-47	<b>0.854</b>	-0.212	-0.154	0.360
BDE-100	<b>0.879</b>	-0.139	-0.198	0.349
BDE-99	<b>0.580</b>	<b>0.575</b>	-0.428	-0.070
BDE-154	<b>0.964</b>	-0.155	-0.068	0.147
BDE-153	<b>0.520</b>	0.060	0.456	0.485
BDE-183	0.252	0.562	-0.195	-0.301
BDE-209	<b>0.743</b>	0.255	-0.128	-0.445
syn-DP	<b>0.965</b>	-0.215	-0.063	0.091
anti-DP	<b>0.925</b>	-0.049	-0.062	0.145
PBEB	0.318	<b>0.574</b>	0.271	0.128
HBB	<b>0.956</b>	-0.128	0.024	-0.026
TBB	<b>0.942</b>	-0.251	0-0.009	-0.047
BTBPE	<b>0.930</b>	-0.001	0.141	-0.298
TBPH	<b>0.856</b>	-0.034	0.048	-0.317
DBDPE	<b>0.944</b>	-0.186	-0.015	-0.179
TOC	0.293	<b>0.608</b>	-0.315	0.361
BC	-0.036	<b>0.646</b>	-0.372	0.146
Eigen value	10.468	2.513	1.625	1.277
% of variance	55.095	13.228	8.554	6.722
Cumulative %	55.095	68.324	76.878	83.600



6.72% of total variance in HFRs dataset and did not show high loading on any congeners.

### 3.6. Correlation analysis

A Spearman's rank correlation coefficient analysis was applied to the whole dataset of HFRs to investigate the inter- and intra-relationship among different HFRs together with TOC and BC contents in the soil. The Spearman's rank correlation coefficient matrices of the individual compound have been shown in Fig. 4 and summarized in Table S6. The % TOC and BC content in soil in this study ranged from 0.099–2.473 (median 0.877), and 0.025–0.586

(median 0.105), respectively. The result indicated that TOC was moderately and positively correlated with penta-BDEs ( $R = 0.601$ ,  $p < 0.05$ ) and octa-BDEs ( $R = 0.543$ ,  $p < 0.05$ ), while it was weakly and positively correlated with deca-BDE ( $R = 0.424$ ,  $p < 0.05$ ). This suggested the commercial penta- and octa-BDEs have more or less similar source. Likewise, slightly weak correlation of deca-BDEs indicates de-bromination of high-brominated PBDEs (Gevao et al., 2010). A similar correlation of TOC with deca-BDE has been previously reported in soil from e-waste dumping sites in Ghana (Akortia et al., 2017). However, none of the HFRs analyzed in soil were related with BC, suggesting no or little role of BC in the distribution of HFRs.

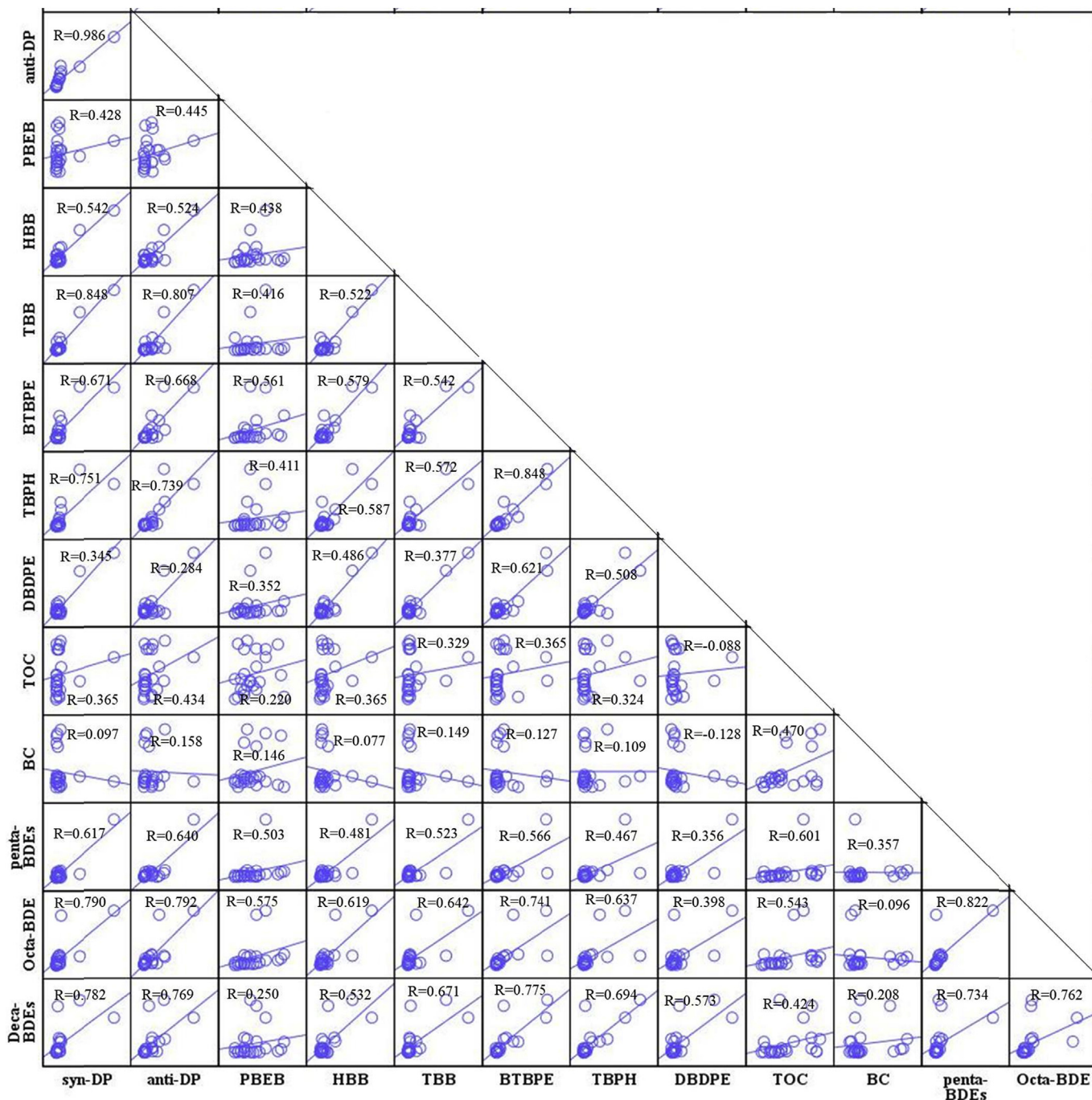


Fig. 4. Scatter plots of HFRs compound showing spearman's rank correlation between HFRs, TOC and BC in soil.

Penta-BDE was significantly and positively correlated with octa-BDE ( $R = 0.822, p < 0.05$ ) and deca-BDE ( $R = 0.734, p < 0.05$ ), while only octa-BDE was positively and significantly correlated with deca-BDEs ( $R = 0.762, p < 0.05$ ). Octa-BDE was also positively correlated with BTBPE ( $R = 0.741, p < 0.05$ ), TBB ( $R = 0.642, p < 0.05$ ) and TBPH ( $R = 0.637, p < 0.05$ ). Both syn-DP and anti-DP were significantly and positively correlated with most HFR congeners analyzed in the soil. Syn-DP and anti-DP were positively and significantly correlated with octa-BDEs ( $R = 0.790$  and  $0.792, p < 0.05$ ), deca-BDEs ( $R = 0.782$  and  $0.769, p < 0.05$ ) and penta-BDEs ( $R = 0.617$  and  $0.640, p < 0.05$ ), respectively. Syn-DP and anti-DP were also significantly and positively correlated with TBB ( $R = 0.848$  and  $0.807, p < 0.05$ ), BTBPE ( $R = 0.671$  and  $0.668, p < 0.05$ ), TBPH ( $R = 0.751$  and  $0.739, p < 0.05$ ) and HBB ( $R = 0.542$  and  $0.524, p < 0.05$ ), respectively. This indicates that DPs, TBB, BTBPE, TBPH, and HBB can have a similar source as well as environmental fate, however, not the same as those of DBDPE and PBEB. A similar finding has been reported previously in biota from e-waste recycling sites in China (Zhang et al., 2011).

### 3.7. Air-soil exchange study

The air-soil exchange study based on fugacity fraction of individual HFR has been shown in Fig. 5. The result indicates that soil to air fugacity for all HFR irrespective of study sites were less than 0.05 which is much lower than equilibrium value of 0.5. This indicates the air and soil are far from equilibrium, and deposition and net transport from air to soil are predominant. This might be because of ongoing contamination of outdoor air by indoor air and exhausted air from the house together with pre-background air contamination. Among HFR congeners, DPs and NBFs showed less fugacity fraction ( $<0.005$ ) demonstrating much far from equilibrium because of their higher air partitioning coefficient ( $K_{OA}$ ). This was further supported by weak correlation of TOC and BC with many HFR congeners. A similar finding has been reported previously from Stockholm Sweden (Newton et al., 2015).

### 3.8. Soil-air partitioning

TOC and BC play a significant role in the dissemination of POPs especially SVOCs. In this study, temperature dependent  $K_{OA}$  and  $K_{BC-A}$  as a function of  $K_{SA}$  was studied by absorption model given in

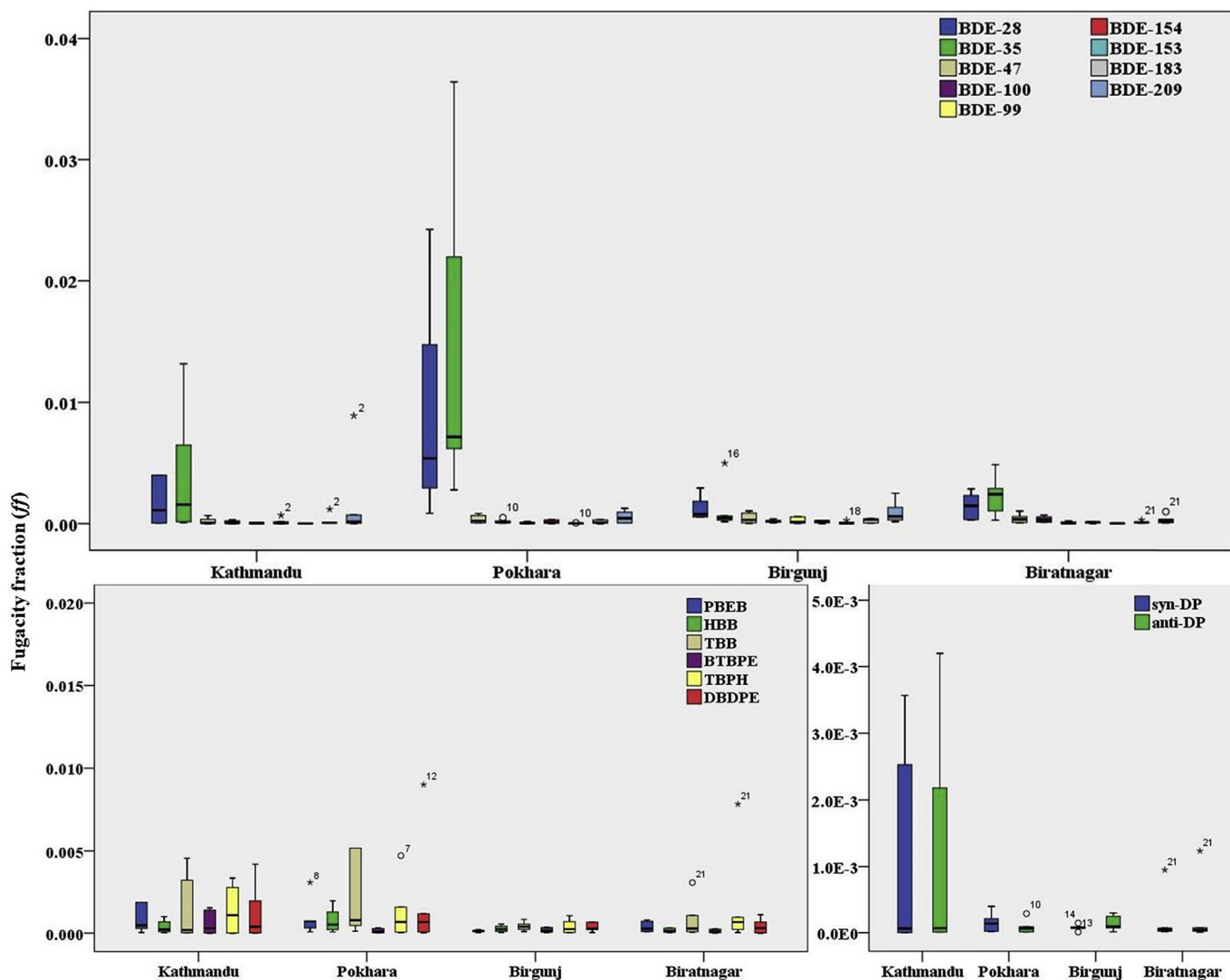
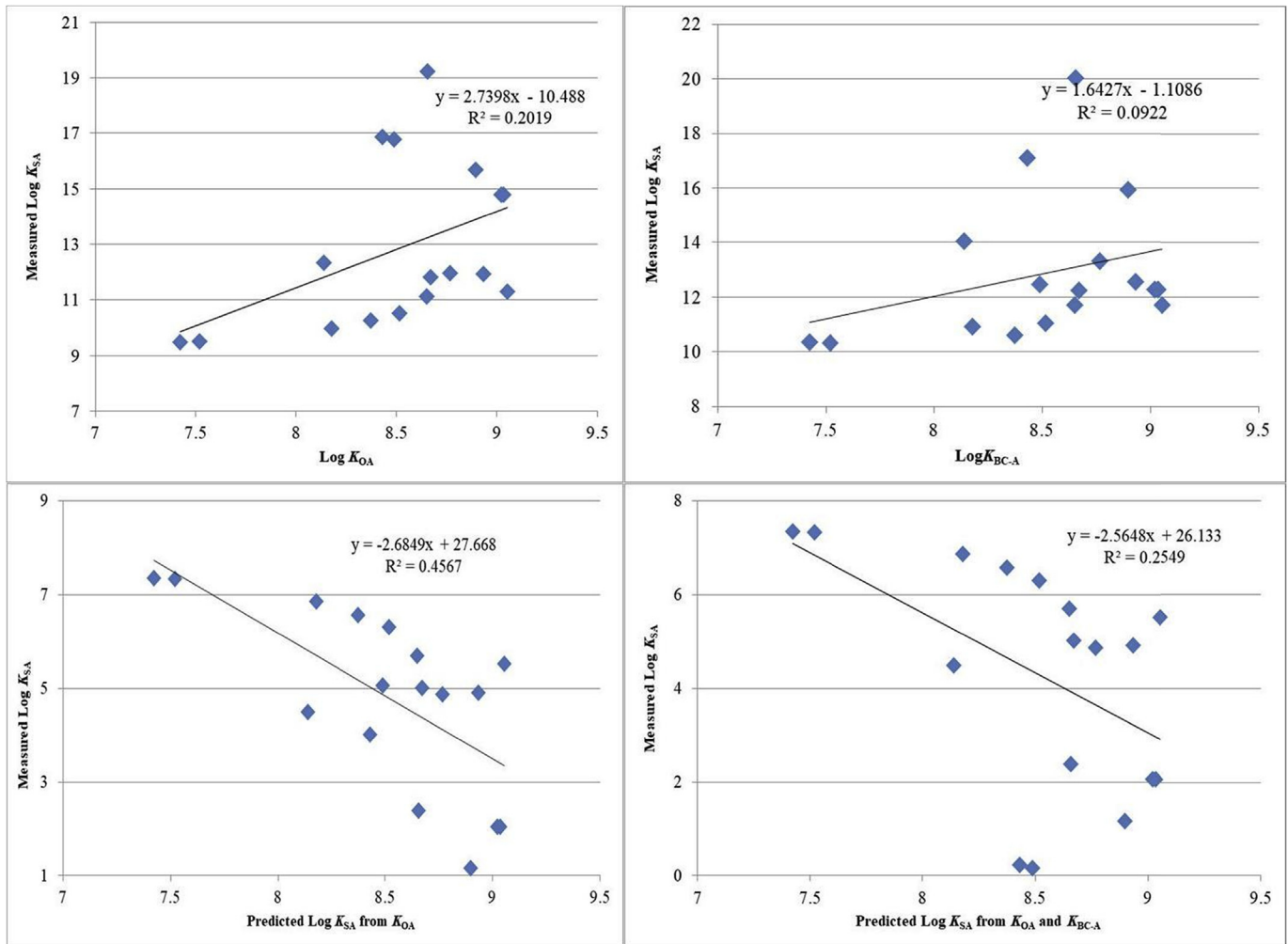


Fig. 5. Box and whisker plot showing fugacity fraction of HFR congeners in Kathmandu, Pokhara, Birgunj and Biratnagar.



**Fig. 6.** Influence of  $\text{Log } K_{\text{OA}}$  and  $\text{Log } K_{\text{BC-A}}$  on measured  $\text{Log } K_{\text{SA}}$  (top graph), and comparison of measured and predicted  $K_{\text{SA}}$  (bottom graph).

Eqs (5) and (6). No significant correlation ( $R^2 = 0.201$ ,  $p < 0.05$ ) was seen between  $\text{Log } K_{\text{SA}}$  and  $\text{Log } K_{\text{OA}}$  (Fig. 6). Likewise,  $\text{Log } K_{\text{SA}}$  and  $\text{Log } K_{\text{BC-A}}$  was also poorly correlated ( $R^2 = 0.092$ ,  $p < 0.05$ ) to each other, proposing neither octanol-air partition coefficient ( $K_{\text{OA}}$ ) nor black carbon partition coefficient ( $K_{\text{BC-A}}$ ) is suitable surrogate for SOM, hence cannot anticipate soil-air partitioning for HFRs or can foresee to a lesser extent.

Further, to model the fate of HFRs as a function of absorption by SOM, we compared measured  $K_{\text{SA}}$  from Eq (4) with that predicted by Eqs (5) and (6). The results showed no significant correlation between measured and predicted  $K_{\text{SA}}$  (Fig. 6). Both predicted  $K_{\text{SA}}$  from  $K_{\text{OA}}$  and  $K_{\text{BC-A}}$  showed weak correlation with measured  $K_{\text{SA}}$ , suggesting absorption by SOM has no or little role in soil-air partitioning for HFRs in Nepalese soil.

#### 4. Conclusions

This study investigated the environmental concentration and fate of 9PBDEs, 2 DPs and 6 NBRs in soil from four major cities of Nepal. Generally, the concentration of DBDPE measured high in soil than PBDE and DP. High level of DBDPE and DP were most prominent in Kathmandu while an elevated level of PBDEs was seen in Pokhara. The sources of an elevated level of PBDEs were identified as the contributions from commercial penta-, octa- and -deca-BDEs formulations. Likewise, high level of DBDPE was linked with

the use of wide variety of consumer product and building materials. The sources of high DPs in soil might have originated from long-range atmospheric transport from remote areas. The fugacity fraction of individuals HFR calculated for air-soil exchange study confirms the deposition and net transport from air to the soil is prevailing. The soil-air partitioning estimation indicated neither  $K_{\text{OA}}$  nor  $K_{\text{BC-A}}$  is a reasonable surrogate for SOM. Further, absorption by SOM has no or little role in the soil-air partitioning of HFR in Nepalese soil.

#### Conflict of interest

The authors declare no competing financial interest.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.envpol.2017.10.104>.



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