Organophosphate ester flame retardants in Nepalese soil: Spatial distribution, source apportionment and air-soil exchange assessment

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HIGHLIGHTS

- Eight OPFRs detected in soil with 100% detection frequency.
- Very high concentration of TMPP; accounting for 35–49% of $\sum$OPFRs.
- Fugacity fraction indicated strong influence of soil pollution on air concentration.
- Weak correlation of TOC/BC with OPFRs suggested little or no role on soil OPFRs.

GRAPHICAL ABSTRACT
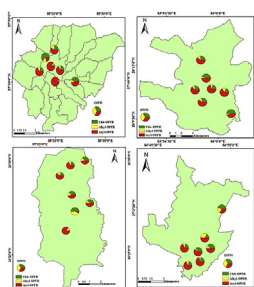
ABSTRACT

Despite soil being the major terrestrial environmental reservoir and one of the significant sinks for many hydrophobic organic compounds including organophosphate ester flame retardants (OPFRs), limited information is available about concentration and fate of OPFRs contamination in urban soil in general and especially in case of Nepal. This study investigates the environmental concentration, spatial distribution and source apportionment of eight OPFRs in surface soil (n = 28) from four major cities of Nepal with special interest on air-soil exchange. Overall, significantly high concentrations of $\sum_8$OPFR were measured in soil ranging from 25–27,900 ng/g dw (median 248 ng/g dw). In terms of compositional pattern, tris(methyl phenyl) phosphate (TMPP) was the most abundant phosphorus chemical in soil, followed by tris(2-chloroisopropyl) phosphate (TCIPP), and accounted for 35–49% and 8–25% of $\sum_8$OPFRs, respectively. The high level of these OPFRs was attributed to local sources as opposed to transboundary influence from remote areas. A Spearman's rank correlation analysis exhibited weak correlation of $\sum_8$OPFRs with TOC ($Rho = 0.117$, p < 0.05) and BC ($Rho = 0.007$, p < 0.05), suggesting little or no influence of TOC and BC on the concentration of $\sum_8$OPFRs. The fugacity fraction (ff) results indicated a strong influence of soil contamination on atmospheric level of OPFRs via volatilization.

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1. Introduction

Organophosphate ester flame retardants (OPFRs) are groups of man-made chemicals broadly utilized as flame retardants (FRs), plasticizers, as well as antifoaming agents and hydraulic fluids in

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many households and industrial products (Moller et al., 2012). Halogenated-OPFRs, for example, tris(2-chloroethyl) phosphate (TCEP), tris(2-choroisopropyl) phosphate (TCIPP) and tris(1,3-dichloroisopropyl) phosphate (TDCIPP) are predominantly used as FRs, while non-halogenated OPFRs such as 2-ethylhexyl diphenyl phosphate (EHDPHP), tris(methyl phenyl) phosphate (TMPP), and triphenyl phosphate (TPHP) are utilized as plasticizers in different applications (Marklund et al., 2003). Tri (2-ethylhexyl) phosphate (TEHP) is mainly used as a plasticizer in PVC in low temperature applications. It is also used in human clothing as FRs (OEHHA, 2011). After the worldwide restriction and ban on the utilization of polybrominated diphenyl ethers (Wei et al., 2015), the consumption and utilization of OPFRs in different consumer items, have significantly increased in recent year. A few OPFR compounds are released to the environment during industrial processes (Bacaloni et al., 2008). Furthermore, OPFR is significant constituents of Firemaster 550 (including TPHP), which constitute about 60% of the commercial FRs mixture (Hammel et al., 2016).

OPFRs are one of the significant groups of environmental pollutants occurring in different environmental matrices as they are used extensively in various consumer products and building materials in high amounts (van der Veen and de Boer, 2012; Salamova et al., 2014; Wei et al., 2015). They may undergo long-range atmospheric transport (LRAT) (Salamova et al., 2014; Gramatica et al., 2016), and have been known for various toxicological effects (Belcher et al., 2014; Pillai et al., 2014; Noyes et al., 2015). A number of studies have distinguished different toxicological effect on humans and animals attributed to OPFRs exposure (WHO, 1998, 2000; Meeker and Stapleton, 2010; van der Veen and de Boer, 2012; Araki et al., 2014; Hou et al., 2016). For instance, Tri-n-butyl phosphate (TNBP), TPHP, and TCEP are known to cause neurotoxic effects in human on chronic exposure (van der Veen and de Boer, 2012; Araki et al., 2014). TCIPP, TDCIPP, and TCEP, are suspected to be carcinogenic (WHO, 1998, 2000; Hou et al., 2016). In addition, an elevated level of TDCIPP and TPHP in house dust is reported to have a significant impact on hormone levels and semen quality (Meeker and Stapleton, 2010).

Generally, OPFRs are utilized as non-reactive additives in consumer products, and therefore easily released from these products to the surrounding environment (Marklund et al., 2003). Thus, the occurrence and fate of OPFRs in different environmental matrices have attracted increasing attention from both the public and researchers across the globe (van der Veen and de Boer, 2012; Gao et al., 2016; Hammel et al., 2016; Luo et al., 2016; Wu et al., 2016). Widespread use of OPFR-added electronic devices and commercial products could also lead to elevated levels of OPFR and are therefore ubiquitous pollutants in urban environments (Abdallah and Covaci, 2014; Cao et al., 2014; Li et al., 2014; Yang et al., 2014; Kucharska et al., 2015; Ding et al., 2016a, b; Gao et al., 2016; Wu et al., 2016). However, information on the contamination level, sources, and fate of OPFR contamination in solid matrices including soil is limited. Relatively, higher organic carbon-water partitioning coefficients (K_{oc}) of some OPFR chemicals, their accumulation in soil is obvious. The possible sources of OPFRs in soil includes the application of sewage sludge, wastewater application for irrigation, disposal of FRs plastics in landfills, hydraulic fluids discharged, and dry and wet deposition processes (Muir, 1984; Stachel et al., 2007; Passuello et al., 2010). Moreover, the release of OPFR from buildings and traffic emission into the air could also influence soil-OPFR (Marklund et al., 2005b). Soil is composed of mineral constituents and its organic matter content is the major terrestrial environmental reservoir and one of the vital sinks for aqua-phobic organic pollutants, especially OPFR (van der Veen and de Boer, 2012; Wei et al., 2015).

Be that as it may, only sparse information is accessible about environmental concentration and fate of OPFRs in urban soil in general (Fries and Mihajlovic, 2011; Mihajlovic et al., 2011; Mihajlovic and Fries, 2012), and particularly in case of Nepal, located between world's two most populous countries India and China. It is one of the world's poorest and most appealing nations for the adventure traveler. Despite, a couple of previous studies that reported extensive contamination of halogenated flame retardants (Yadav et al., 2017a), organochlorine (Yadav et al., 2016) and polychlorinated biphenyls (Yadav et al., 2017b, c) in air and soil, detailed understanding of OPFR contamination in soil environment is lacking. Therefore, the present study aims to investigate the environmental occurrence, profile and spatial distribution of OPFR in surface soil from four major cities of Nepal. Additionally, the air-soil exchange was assessed to know the potential impact of soil pollution on atmospheric level of OPFRs and vice versa.

2. Materials and methods

Detailed descriptions of the materials and methods are given in Supporting Information.

2.1. Study area and sampling

Four major cities (Kathmandu, Pokhara, Birgunj, and Biratnagar) of Nepal were selected for the study (Fig. S1, Supporting information). The details about sampling locations and collection procedure are described elsewhere (Yadav et al., 2017b). Briefly, about 50 g of surface soils (0–15 cm depth, vegetation removed) at 28 sites (n = 28) within the selected cities were collected during August-October 2014 using stainless steel scoops. Each soil sample was a composite of 3 sub-samples which was collected and mixed from a radius of 5 m in the different direction. The soil samples were then wrapped in aluminum foil, packed into sealed polythene bags and transported to the laboratory kept in the ice bag. After being freeze-dried at the laboratory, they were ground to powder, sieved through 500 μm sieves, and stored at −20 °C until analysis.

2.2. TOC and BC analysis

About 2–3 g of freeze dried, sieved and homogenized soil samples were used for TOC analysis. The soil samples were treated with 3 ml of HCl (3%) and kept for 8 h to remove inorganic carbon. Thereafter, the soil samples were washed thrice with Milli-Q water and dried in an oven at 45 °C. A portion of dried soil was utilized for TOC analysis utilizing Elemental Carbon−Hydrogen−Nitrogen Analyzer (Elementar VARIO EL III). BC in soil samples was measured using the chemo-thermal oxidation (CTO-375) technique described elsewhere (Gustafsson et al., 2001; Elmquist et al., 2008). In brief, 2−3 g of soil was burnt in the muffle furnace at 375 °C for 18 h under continuous air flow and analyzed by Elemental CHN analyzer. Prior to analysis, the burnt soil was mixed with 3 ml HCl (1 N) and washed thrice with Milli-Q water.

2.3. Sample preparation and extraction

Freeze dried, sieved and homogenized soil samples (10 g) were soxhlet extracted with DCM for 24 h. A known amount of 5 μL (200 ng/μL) deuterated tris (2-chloroethyl) phosphate (TCEP-d12) was spiked to each sample as surrogate standard before extraction. Additionally, copper granules were added to the round bottle flask before extraction to remove the elemental sulfur present in soils. Copper granules were pre-washed and activated with hydrochloric acid prior to adding to the flask. The sample extract was reduced by the rotary evaporator (Heidolph 4000, Germany) and was solvent exchanged to hexane with a volume of 0.5 mL. The extract was then

passed through Supelclean Envi Florisil SPE column tubes 6 mL (1 g) (SUPELCO, USA). Prior to fractionation, Florisil® cartridges were pre-washed with 6 mL ethyl acetate, 6 mL hexane/DCM (8:2, v/v), and 10 mL hexane to clean and condition the adsorbent. After transfer to the SPE column, a first fraction was eluted with 6 mL 8:2 Hex: DCM and was discarded. The second fraction that contained target OPFRs was eluted with 20 mL ethyl acetate, evaporated until dryness under nitrogen flow, and the residue was re-dissolved in 200 μL of *iso*-octane. The resulting fraction was transferred to GC vials for GC-MS analysis. Prior to GC-MS injection, a known amount (1000 ng) of hexamethyl benzene (HMB) was added as internal standard for quantification.

2.4. GC-MS analysis

OPFR analysis was performed in an Agilent 7890 A GC coupled with an Agilent 7000 A GC/MS single quadrupole, with a DB5-MS capillary column (30 m × 0.25 mm i. d. × 0.25 μm film thicknesses) in EI mode. The temperature of transfer line and ion source was maintained at 280 °C and 230 °C, respectively. The GC oven temperature started at 60 °C for 1 min, increased to 220 °C at a rate of 30 °C min-1 (held for 0 min), then to 300 °C at a rate of 5 °C min-1 (held for 15 min). Eight OPFRs such as TCEP, TDCIPP, TCIPPs (mix of three isomers), TNBP, TPHP, EHDPHP, TEHP and TMPPs (mix of three isomers) were targeted. The specific parameters for the target compounds are shown in Table S1.

2.5. QA/QC

Ten laboratory blanks were extracted and analyzed together with soil samples to assess the possible contamination. The level of OPFRs detected in laboratory blanks ranged from 0.48–9.10 ng/g (Table S2). The method detection limit (MDL) was calculated as the mean plus 3 times the standard deviation of all the blank samples. When the OPFR compounds were not detected in the blank, the MDL was calculated as 3 times signal to noise ratio obtained from the lowest spiked standard. The MDL of OPFR ranged from 0.51–17.1 ng/g. The recovery standard for TCEP-d12 in all samples ranged from 85–124%. The concentrations of target OPFR in this study were corrected for blanks, but not corrected for recovery. Detailed about QA/QC is given in SI.

3. Results and discussion

3.1. Concentration of OPFRs

In this study, all 8 target OPFRs were detected in soil with 100% detection frequency (DF). The concentrations of $\sum_8$OPFRs in surface soil ranged from 25–27,900 ng/g dw (median 248 ng/g dw). The aryl-OPFR was the highest phosphorus chemical measured in soil, followed by chlorinated- and alkylated-OPFR, and ranged 7.3–25600 ng/g (median 162 ng/g dw), 12.7–1460 ng/g (median 55.3 ng/g dw) and 4.9–911 ng/g (median 31.4 ng/g dw), respectively (Table 1). Separately, TMPP was the most abundant phosphorus chemical measured in soil, followed by TPHP, EHDPHP, TCIPP, TCEP and TNBP, and ranged from 1.6–25300 ng/g dw (median 113 ng/g dw), 5–147 ng/g dw (median 25.3 ng/g dw),0.59–114 ng/g dw (median 23.2 ng/g dw),0.64–991 ng/g dw (median 21.5 ng/g dw), nd-83.7 ng/g dw (median 21.2 ng/g dw) and 0.77–53.3 ng/g dw (median 16.9 ng/g dw), respectively.

### 3.2. Intercity variation and profile of OPFRs

The statistical summaries of 8 OPFRs, including three chlorinated, three arylated and two alkylated-OPFRs analyzed in soil in

Table 1
Statistical summary of OPFRs measured in soil (ng/g) from Nepal.

OPFRs	OPFRs concentrations (ng/g)				
	Min	Max	Median	Mean	Std. Dev.
TNBP	0.77	53.3	16.9	18.1	8.25
TCEP	nd	83.7	21.2	29.5	23.4
TCIPPs	0.64	991	21.5	103	195
TDCIPP	12.1	390	12.6	33.4	71.8
TPHP	5.06	147	25.3	35.8	28.6
EHDPHP	0.59	114	23.2	32.2	25.9
TEHP	4.14	858	14.5	102	222
TMPPs	1.64	25300	113	1260	4820
$\sum$Chlor-OPFRs	12.7	1460	55.3	165	290
$\sum$Alkyl-OPFRs	4.91	911	31.4	120	230
$\sum$Aryl-OPFRs	7.29	25600	162	1328	4870
$\sum$OPFRs	24.9	27900	248	1610	5390

this study are presented in Table S3. The concentration of $\sum_8$OPFRs in the four cities ranked from highest to lowest in the order: Kathmandu > Biratnagar > Birgunj > Pokhara. Surface soil in Kathmandu exhibited 2–3 times higher $\sum_8$OPFRs level than other cities. The level of $\sum_8$OPFRs ranged from 204–27500 ng/g dw (median 662 ng/g dw), 75–6980 ng/g dw (median 244 ng/g dw), 38–636 ng/g dw (median 233 ng/g dw) and 183–470 ng/g dw (median 221 ng/g dw) in Kathmandu, Biratnagar, Birgunj, and Pokhara, respectively (Fig. 1). In this study, fairly high level of $\sum_8$OPFRs in Kathmandu is because Kathmandu is the most populated and capital city of the country, which consequently consumes large quantities of consumer products and building materials. Previously, high level of $\sum$OPFRs has also been reported in indoor air and dust from Kathmandu (Yadav et al., 2018). Next to Kathmandu, the second highest $\sum_8$OPFRs was measured in Biratnagar, which could be due to a large number of industries and factories located in Biratnagar. Biratnagar is known as the industrial capital city of Nepal and has the largest number of medium and small scale industries. OPFRs are utilized in broad range of application as additives. Hence, significant emission to the environment can occur during industrial and manufacturing process, leaching and abrasion of the products to which they are added. Biratnagar being the second most densely populated city after Kathmandu could also influence the OPFR level in soil (CBS/NPCS, 2011; Li et al., 2014; Cui et al., 2017a; He et al., 2017). The concentration of $\sum_8$OPFRs together with individual OPFR measured in soil in this study was compared with previous studies around the world (Fig. 2 and Table S4). Although, limited information is available on contamination level of OPFRs in soil matrix, the level of $\sum_8$OPFRs in soil in this study was 8–20 times higher than those reported in urban soil from China (32 ng/g) and Germany (18.9 ng/g) (Fig. 2 and Table S4) (Mihajlovic et al., 2011; Jian-Xia et al., 2014). Except for Kathmandu, the concentration of $\sum_8$OPFRs in the soil was comparable with OPFR level reported in soil from residential areas in China (180 ng/g)(Cui et al., 2017a). However, the levels of $\sum_8$OPFRs in soil in this study were half of those reported in commercial areas, university campus soil, and plastic waste treatments facilities in China (Wan et al., 2016; Cui et al., 2017a, b) (Fig. 2 and Table S4). Moreover, David and Seiber (1999) also reported significantly high level of $\sum$OPFRs (nd-136000 ng/g) in Air Force Base (AFB) soil of the USA. Only soil from Kathmandu measured higher concentration of $\sum_8$OPFRs which was 1.5–2 times higher than that reported in Chinese urban soil (Cui et al., 2017a). High fluctuation of OPFRs in different regions is occasionally documented. Dirtu et al. (2012) opined that the fluctuation could be due to multiple reasons since OPFRs are not only used as FRs but also as plasticizers. Moreover, difference in regulation and restriction from one region to other could also influence soil OPFR (Dirtu et al., 2012).
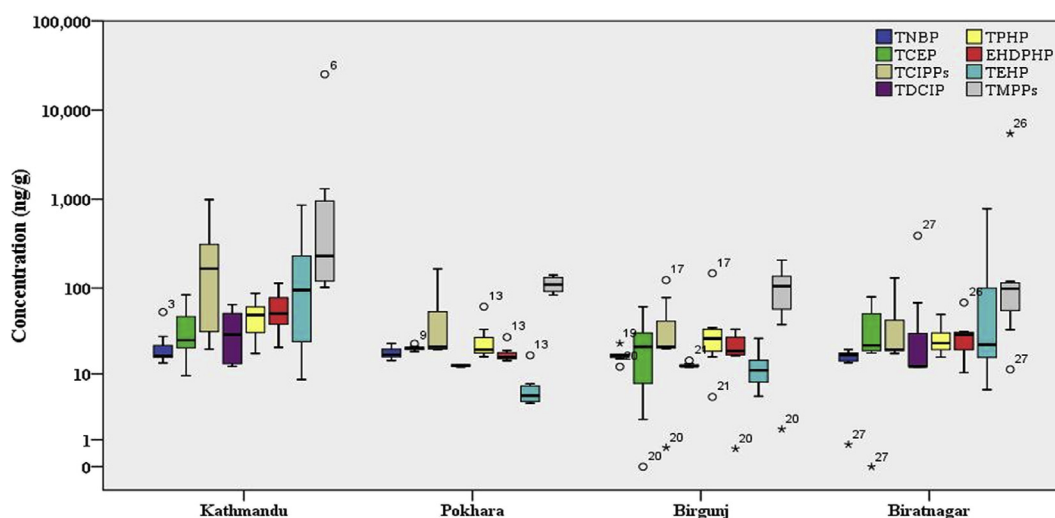
Fig. 1. Box and whisker-plots showing lower and upper concentration of Individual OPFR in soil (ng/g). The central box represents the concentration from 25 to 75 percentile. The middle bold line represents the median value. The asterisk/stars are the extreme outliers that are >3-times beyond interquartile range. The concentration in Y-axis is in logarithmic scale.

The profile of individual OPFR measured in the soil in this study is shown in Fig. 3 and Fig. S2. It is evident from Fig. 3 that the individual component of OPFR was mostly controlled by TMPP, followed by TCIPP, and accounted for 35–49% and 8–25% of $\sum_8$OPFRs, respectively. Soil samples in Kathmandu showed slightly different pattern than rest of the Nepalese cities. Next to TMPP, the concentration of $\sum$OPFRs in Kathmandu was essentially contributed by TCIPP and TEHP, and accounted for 25% and 14% of $\sum_8$OPFRs. High proportions of TCIPP in Kathmandu suggest their wide application in Nepalese consumer items such as furniture, textiles, electronic and building materials to meet flammability standards (van der Veen and de Boer, 2012). Higher proportions of TCIPP have been also reported in air in the Nepalese cities (Yadav et al., 2017d). High amounts of TEHP in soil in Kathmandu indicate traffic emission could be as possible source (Marklund et al., 2005b). The concentration of TMPPs measured in soil (98–230 ng/g) was 2–3 times greater than those measured in the residential, commercial and roadside soil in China (Cui et al., 2017a). Likewise, TMPPs level observed in soil in this study was 4–5 times lower than that reported in AFB soil of the U.S. (nd-130,000 ng/g) (David and Seiber, 1999). The significantly high level of TMPP in the soil in this study might be due to release from end point use of plastic-derived consumer materials as no record of other uses of OPFR in Nepal is available (Yadav et al., 2017d). TMPP is predominantly used as the plasticizer in different kinds of plastic products, rubber, floor cleaning agent, wallpapers and as the additive in cables and electrical appliances (van der Veen and de Boer, 2012). It is also widely applied as extreme pressure lubricant and as non-flammable fluid in the hydraulic fluid and motor oil (Solbu et al., 2005). Cho et al. (1996) recommended plastic film made of PVC is important sources of TMPP in agricultural soil. David and Seiber (1999) also found the high level of TMPPs in AFB (US) soil related to leakage from hydraulic fluid. In a similar study, Yadav et al. (2018) also found the discharge from end point use of consumer products and building materials to be the principal source of TMPP in surface soil in the Kathmandu Valley.

Among chlorinated-OPFRs, TCIPP and TCEP were abundantly detected in soil. The TCEP level (21.2 ng/g) measured in soil in this study was 4–5 times higher than those measured in urban soil from Germany (4.96 ng/g) and China (5.61 ng/g) (Mihajlovic et al., 2011; Jian Xia et al., 2014) (Table S4). TCEP is known to be used in polyurethane foam, rubber, and textile coatings, and upholstery

employed in vehicles cabin (European Commission, 2009; Xu et al., 2016; Wu et al., 2016). Furthermore, atmospheric deposition by rain could also contribute the significant level of TCEP in soil (Mihajlovic et al., 2011). Hence, this range of TCEP in the soil in this study could also be released from consumer materials (polyurethane foam, rubber, textile coatings and upholstery). Moreover, low degradation potential of TCEP may also cause TCEP to remain in the environment for longtime (Gao et al., 2016; Luo et al., 2016; Wei et al., 2015). Although the use of TCEP in baby products is restricted in many developed countries including the USA because of their carcinogenic impact, TCEP application in baby product in developing countries including Nepal cannot be neglected as it is not regulated yet in Nepal (Gao et al., 2016; Wu et al., 2016). Worldwide, China being the most exporting nation of toys and baby products also lacks regulation on TCEP. More recently, the elevated level of TCEP in Chinese soil was linked with the utilization of TCEP in baby toys and other similar products (Cui et al., 2017a). High concentration of TCEP in soil could also results from secondary outdoor emission sources such as diffusion from plastic materials, use of wastewater for irrigation, the application of sewage sludge, the disposal of flame retardant plastics in landfills and river flooding (Passuello et al., 2010; Mihajlovic et al., 2011).

Next to TCEP, TCIPPs was the second most abundant chlorinated phosphorus chemical measured in soil and ranged from 1–991 ng/g (median 21.5 ng/g). This concentration of TCIPPs is 7–20 times higher than those reported in university campus's soil from Germany (1.23 ng/g) (Mihajlovic et al., 2011) and residential soil from China (1 ng/g) (Cui et al., 2017a). The level of TCIPPs measured in soil in this study is consistent with previous studies reported in surface soil from roadside and plastic waste treatment facilities in China (Jian-Xia et al., 2014; Wan et al., 2016). TPHP is less soluble in water and is mainly associated with particles (Mihajlovic et al., 2011). The TPHP level (5–147 ng/g) measured in this study was about 30–40 times lower than reported in AFB soil (US) (nd-6000 ng/g) (David and Seiber, 1999), but higher than those reported in urban soil from China and Germany (Mihajlovic et al., 2011; Jian Xia et al., 2014).

3.3. Spatial distributions of OPFRs

The spatial distributions of $\sum_8$OPFRs together with chlorinated-, alkyl, and arylated-OPFRs measured in the soil in this study are
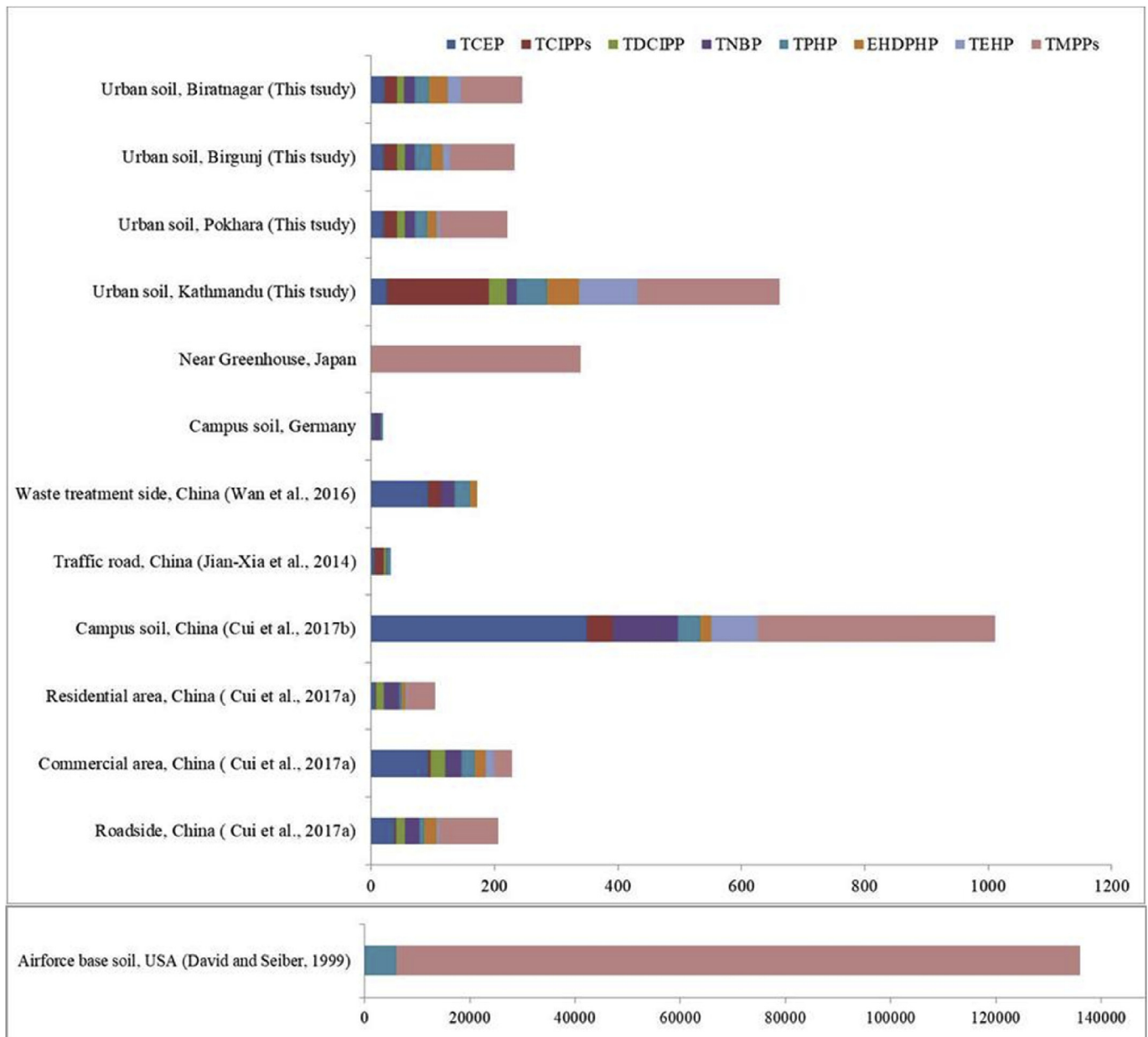
Fig. 2. Comparison of OPFRs in soil in this study with previous studies from the world. Concentration on the x-axis is given in ng/g.
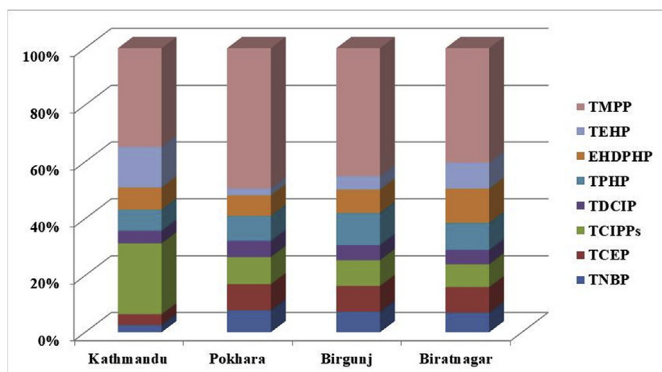

Fig. 3. Profile of OPFRs showing median % contribution of individual OPFR to $\sum$OPFRs in soil.

shown in Fig. 4 and Fig. S3. It is evident from Fig. S3 that the levels of $\sum_8$OPFRs were highly abundant in Kathmandu and Biratnagar, while less so in Pokhara and Birgunj. Extremely high-level $\sum_8$OPFRs was measured at KTS6 (26800 ng/g) in Kathmandu (Fig. S3). Higher concentrations of $\sum_8$OPFRs were also prevalent at BTS5 (6540 ng/g) and BTS6 (988 ng/g) in Biratnagar, and KTS4 (1750 ng/g), KTS3 (1710 ng/g), and KTS5 (1390 ng/g) in Kathmandu. KTS 6 is an intense traffic area, KTS4 is the urban commercial area, and KTS3 is close proximity to the industrial area. Likewise, BTS6 and BTS5 in Biratnagar were also classified as high traffic area together with the urban-residential area. The lowest concentration of $\sum_8$OPFRs was measured at BRS 6 (73 ng/g) and BRS 7 (207 ng/g) in Birgunj, BTS4 (128 ng/g) in Biratnagar, and PKS 1 (197 ng/g) and PKS2 (194 ng/g) in Pokhara, respectively. BRS6 and BRS7 are the suburban residential area, while PKS1 and PKS2 are urban-tourist area. Likewise, BTS4 is recognized as institutional area. This showed that large variation in concentration of OPFR within the
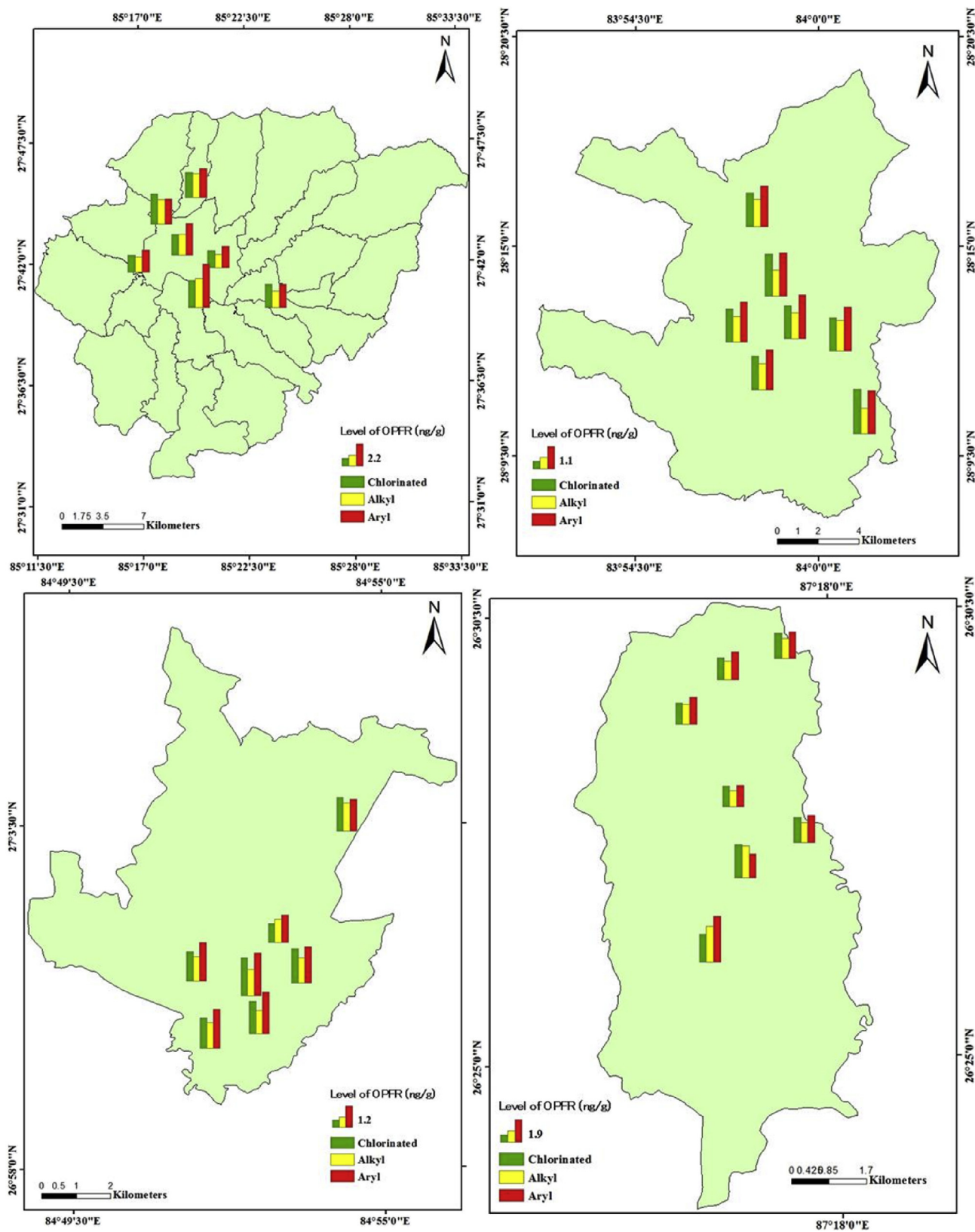
Fig. 4. Spatial distribution map of chlorinated, alkylated and arylated-OPFR in soil samples of Nepalese cities.

same cities. The median concentration of $\sum_8$OPFRs for urban, traffic and industrial sites was higher than that of sub-urban residential sites. This implies that the local sources attributed to high level of OPFRs in soil rather than *trans*-boundary influence (Ren et al., 2008; Bergh et al., 2011). Moreover, TMPP, EHDPHP and TPHP which contributed 65% of the $\sum_8$OPFRs have relatively low vapor pressure but high octanol-air partitioning coefficient (K_{OA}). Thus, the less volatile OPFRs (TMPP, EHDPHP and TPHP) with high K_{OA} (12, 8.3, and 9.8, respectively) tends to adsorb onto particles and can be deposited in soil (WHO, 1991). Thus, the spatial variation within the cities and the high level of particle bound OPFRs indicate that local sources are predominant in urban area of Nepal.

The application of sewage sludge, usage of waste water for irrigation, the disposal of flame retardant plastics in landfills and leakage of hydraulic fluids could also significantly influence OPFR level in soil (Muir, 1984; Stachel et al., 2007; Passuello et al., 2010). Buildings and intensive traffic areas could also release the significant amount of OPFRs in soils through atmospheric deposition (Marklund et al., 2005c; Mihajlovic et al., 2011). Road dust could be another potential source of OPFR to soil as the majority of inner roads in Nepalese cities are unpaved (Gautam et al., 2005; Wang et al., 2014).

3.4. Effect of TOC and BC

Soil organic matter (SOM) is an essential component of soil that plays important role in controlling sorption of POPs (Devi et al., 2015, 2016; Yadav et al., 2016). Previous studies suggested that the concentration of organic pollutants in the soil is significantly related to the content of SOM in soil (Yadav et al., 2016). SOM is 1.5 times the total organic carbon (TOC) in the soil. The TOC content in soil in this study ranged from 0.09 to 2.47% (average 1.11 ± 0.80%). Notwithstanding, BC constitutes just 4% of the TOC in the soil, it is regarded as a 'super-sorbent' in view of its higher sorption capacity (Cornelissen et al., 2005; Nam et al., 2008). The sorption capacity of BC is 10−100 times higher than amorphous organic matter (AOM) and is known to be responsible for large part of sorption/partitioning of POPs (Gustafsson and Gschwend, 1998; Nam et al., 2008). The BC content measured in the soil in this study was in the range of 0.03−0.59% (average 0.17 ± 0.18%). A Spearman's rank correlation analysis exhibited weak relation between $\sum_8$OPFR, TOC ($Rho = 0.117$, $p < 0.05$) and BC ($Rho = 0.01$, $p < 0.05$). This suggests TOC and BC have no or very little influence on the level of OPFRs in Nepalese soil. This might be because of weak binding capacity of OPFR with organic carbon. A similar finding has been reported previously in urban soil from China (Cui et al., 2017a).

3.5. Interrelationship of OPFR chemicals

A Spearman's rank correlation between individual OPFR was applied in the investigation of the association between different compounds (Table S5). EHDPHP was significantly and positively correlated with most of the OPFR chemicals analyzed in soil, for instance, TEHP ($Rho = 0.80$, $p < 0.05$), TDCIPP ($Rho = 0.660$, $p < 0.05$), TPHP ($Rho = 0.621$, $p < 0.05$), TMPP ($Rho = 0.573$, $p < 0.05$) suggesting similar source of the released EHDPHP. Also, EHDPHP was moderately and positively correlated with TCEP ($Rho = 0.490$, $p < 0.05$) and TCIPP ($Rho = 0.530$, $p < 0.05$). Significantly strong correlation of EHDPHP with TPHP in soil showed that substantial sources of TPHP in soil are most likely a result of their co-application with EHDPHP (Environment Agency, 2009). TDCIPP was significantly related with TEHP ($Rho = 0.670$, $p < 0.05$), TCIPP ($Rho = 0.660$, $p < 0.05$) and TPHP ($Rho = 0.550$, $p < 0.05$) (Table S5). This suggests TDCIPP, TEHP, TCIPP, and TPHP have similar source. The chlorinated-OPFRs (TDCIPP and TCIPP) are the substituent of

penta-bromodiphenylether (penta- BDE) and are mostly used in polyurethane foam in furniture and baby product (Dodson et al., 2012; van der Veen and de Boer, 2012). High amounts of TDCIPP have been also reported in child care products in the USA (Stapleton et al., 2011). TCIPP has been used as the replacement for TCEP and is often used in the same products as TDCIPP (van der Veen and de Boer, 2012).

3.6. Source apportionment study

In order to investigate the possible entry of OPFRs in Nepalese soil, principal component analysis (PCA) was performed utilizing OPFRs concentration data. Altogether 3 major PCs were extracted with Eigenvalue greater than 1.0 following the varimax orthogonal rotation method. PC1, PC2 and PC3 accounted 39%, 24.8% and 13.8% of the total variance, respectively (Table S6). The degree of association between each variable shows respective loading factors for individual compound. The loading plots of the first three PC are shown in Fig. 5. PC 1 explained 39% of total variance with high loading on EHDPHP (0.830), TEHP (0.80), TMPP (0.750), TCIPP (0.730) and TCEP (0.650) (Table S6). High loading on EHDPHP, TEHP, TMPP, TCIPP and TCEP indicated their co-occurrence in soil. TEHP and TMPP are common environmental contaminants and are present in all environments (Cristale et al., 2016). TCIPP is the main substituent of TCEP (Schindler and Forster, 2009) and has been used in flexible polyurethane foams for furniture upholstery (Lassen and Lokke, 1999; European Union, 2008) and in PVC wallpaper (Ni et al., 2007). Unlike TNBP, both TCEP and TCIPP are resistant to photodegradation (Regnery and Puttmann, 2010). High loading on TCIPP could also be due to discharge of OPFRs from indoor environment to outdoor environment via diverse physicochemical mechanisms, for instance, ventilation and flushing of dust during wet cleaning (Marklund et al., 2003). EHDPHP is the major constituent of food packaging and paints (US FDA, 2006; Brommer, 2014). ence, factor 1 is identified as combined source of release from consumer materials and food packaging and paints (Environment Agency, 2009).

PC 2 accounted 24.8% of total variance, and is mainly positively driven by high abundance of TDCIPP (0.690), TEHP (0.450), while negatively driven by high abundance of TNBP (−0.860). TDCIPP is mainly used as plasticizers, lacquer and antifoaming agents (Marklund et al., 2005a), while TNBP is one of the significant ingredients (up to 79%) in aircraft hydraulic fluids (ATSDA, 1997). Further, it is widely used as extreme pressure additive and antiwear agent in lubricants, car oil and transmission oil to prevent
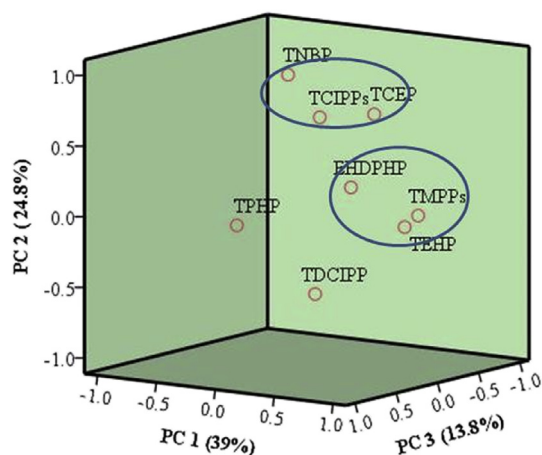

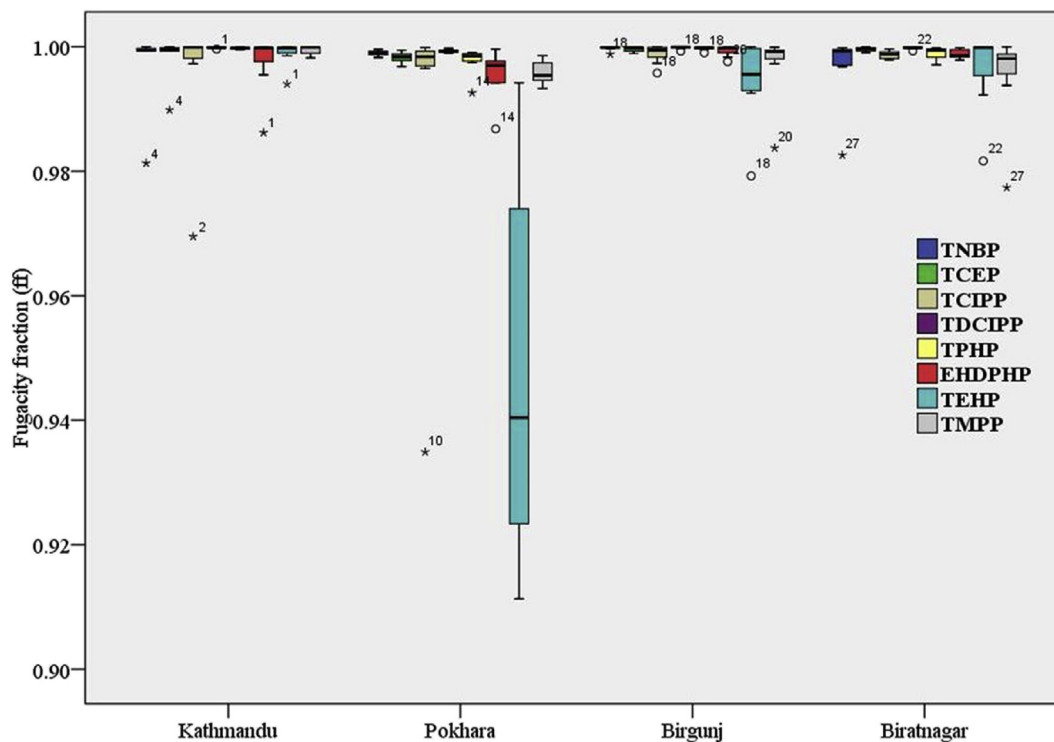**Fig. 5.** Rotated loading plots of PCA for OPFRs in soil of major cities of Nepal.

Fig. 6. Box and whisker plots showing fugacity fraction of eight OPFR four Nepalese cities.

surface damage (ATSDA, 1997; Marklund et al., 2003). TNBP is also significant constituent of plastics, vinyl resins, cellulose esters, lacquers and natural gums (WHO, 1991). Thus, PC 2 is regarded as combined contribution from PVC– made consumer materials, adhesive substance and hydraulic fluid. PC 3 accounts for 13.8% of the total variance and is dominated by TPHP (0.820), which indicates its source to be plastics-induced consumer materials. TPHP is primarily used in unsaturated polyester resins and in PVC for its plasticizing properties (Wei et al., 2015). Additionally, TPHP is ubiquitous contaminant of e-waste and consumer products (Ballesteros-Gómez et al., 2014).

3.7. Air-soil exchange

In order to investigate the potential impacts of soil pollution on air concentration of OPFR and vice versa, air-soil exchange assessment approach (Harner et al., 2001; Ruzickova et al., 2008) was used. The fugacity of OPFR in soil (f_s) was based on the concentrations of OPFR measured in soil in this study and was mathematically estimated as:

$$f_s = C_sRT/0.41\Phi_{OM}K_{OA} \tag{1}$$

where, C_s is the concentration of OPFR in soil (mol/m^3), calculated by using the density of soil about 1430 kg/m^3 (Brady, 1990). R is the universal gas constant (8.310 Pa m^3/mol/K), T is mean daily temperature (K) taken from Meteorological Department and ϕ_{OM} is the fraction of soil organic matter (which is 1.5 times of TOC). K_{OA} is octanol-air partitioning coefficient obtained from Mackay et al. (2006) and presented in Table S7.

Fugacity of OPFR in the air (f_a) was calculated by Eq. (2):

$$f_a = C_{air}RT \tag{2}$$

Where C_{air} is the concentration of OPFR in the air (mol/m^3)

obtained from passive air sampling of each city in previous studies (Yadav et al., 2017d). The fugacity fraction (*ff*) which could indicate the key process that controls the levels of OFR present in the soil and air is calculated from f_s and f_a by Eq. (3)

$$ff = f_s/(f_s + f_a) \tag{3}$$

Air-soil equilibrium is indicated by a fugacity fraction *ff* of 0.5. A value of *ff* < 0.5 represents net deposition, and *ff* above 0.5 indicates net volatilization. Fugacity fractions between 0.3 and 0.7 could not be considered to differ significantly from equilibrium because of the approximations used in calculations (Harner et al., 2001; Ruzickova et al., 2008). The *ff* estimated using Eq. (3) in this study has been shown in Fig. 6. As can be seen from Fig. 6 that the estimated *ff* was 1 or very close to 1, strongly indicating the influence of soil OPFRs on atmospheric level via volatilization. This finding is consistent with the previous study by Yadav et al. (2017c) who also reported the influence of soil PCBs on atmospheric PCBs in Nepalese soil.

4. Conclusions

The results of this study emphasized the actual contamination of OPFRs in Nepalese soil. Overall, higher concentrations of $\sum$OPFRs were measured in all cities. High concentration of OPFRs in soil in this study was attributed to local source rather than transboundary influence from remote areas. TMPP was found to be the most abundant chemical among several classes of OPFRs and was related to endpoint use of plastic made consumer materials. Next to TMPP, soil in Kathmandu showed relatively higher proportions of TCIPP and TEHP among main cities of Nepal. Weak relationship among TOC, BC and $\sum_8$OPFRs suggest TOC and BC have no or little influence on contamination of OPFRs in soil. The fugacity fraction results indicate that net volatilization from soil to air is the principal process in air-soil exchange.

Acknowledgements

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2017.09.112.

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