



Polychlorinated biphenyls in Nepalese surface soils: Spatial distribution, air-soil exchange, and soil-air partitioning

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ABSTRACT

Regardless of the ban on the polychlorinated biphenyls (PCBs) decade ago, significant measures of PCBs are still transmitted from essential sources in cities and are all inclusive ecological contaminants around the world. In this study, the concentrations of PCBs in soil, the air-soil exchange of PCBs, and the soil-air partitioning coefficient (K_{SA}) of PCBs were investigated in four noteworthy urban areas in Nepal. Overall, the concentrations of Σ_{30} PCBs ranged from 10 to 59.4 ng/g dry weight; dw (mean 12.2 ng/g \pm 11.2 ng/g dw). The hexa-CBs (22–31%) was most dominant among several PCB-homologues, followed by tetra-CBs (20–29%), hepta-CBs (12–21%), penta-CBs (15–17%) and tri-CBs (9–19%). The sources of elevated level of PCBs discharge in Nepalese soil was identified as emission from transformer oil, lubricants, breaker oil, cutting oil and paints, and cable insulation. Slightly strong correlation of PCBs with TOC than BC demonstrated that amorphous organic matter (AOM) assumes a more critical part in holding of PCBs than BC in Nepalese soil. The fugacity fraction (ff) results indicated the soil being the source of PCB in air through volatilization and net transport from soil to air. The soil-air partitioning coefficient study suggests the absorption by soil organic matter control soil-air partitioning of PCBs. Slightly weak but positive correlation of measured $\log K_{SA}$ with $\log K_{OA}$ ($R^2 = 0.483$) and $\log K_{BC-A}$ ($R^2 = 0.438$) suggests that both $\log K_{OA}$ and $\log K_{BC-A}$ can predict soil-air partitioning to lesser extent for PCBs.

1. Introduction

Polychlorinated biphenyls (PCBs) are outstanding groups of environmental contaminants. They are known to cause tumor, regenerative and formative sickness, lack in immunity, changes in sensory system, endocrine interruption, gastrointestinal disorder and liver diseases (Faroon and Olson, 2000; Frignani et al., 2007). Since 1930s, they have been broadly utilized in capacitors and transformers as dielectrics, in paints as plasticizers and joint sealants, and in different applications (Wu et al., 2011). Because of high persistency, bioaccumulation potential and high risk associated with PCB (Ritter et al., 1995), Stockholm Convention on Persistent Organic Pollutants (POPs) banned the formulation and application of PCB worldwide in 2004. Regardless of the ban on the PCBs decade ago, significant measures of PCBs are still transmitted from essential sources in urban areas or waste dumping site (Breivik et al., 2007; Diamond et al., 2010; Bogdal et al., 2014; Diefenbacher et al., 2015; Shanahan et al., 2015) and are inclusive ecological pollutants around the world (Meijer et al., 2003; Jaward et al., 2004; Halse et al., 2011). Essential outflows of PCBs are required

to take place predominantly into air (Breivik et al., 2007; Diamond et al., 2010; Bogdal et al., 2014; Diefenbacher et al., 2015; Shanahan et al., 2015), while the soil section, especially high organic matter content may serve as an important interceptor of PCBs (Schuster et al., 2011). It characterizes an intriguing chronicle of PCBs as these are impacted by historical air deposition. Soil organic matter (SOM) may strongly hinder the worldwide dissemination of PCB because of their stronger affinity toward PCBs (Mackay, 2001; Ockenden et al., 2003; Devi et al., 2014).

Soil-air exchange plays a vital role in comprehending the fate and transport of POPs in the environment. A number of studies recommended the use of fugacity for understanding the soil-air exchange phenomenon of POPs (Cousins et al., 1999; Harner et al., 2001; Meijer et al., 2003; Backe et al., 2004; Tasdemir et al., 2012; Sultana et al., 2014). According to Ribes et al. (2003), the soil-air partitioning coefficient may acts as signifier of POPs absorption into SOM and can be projected from octanol-air partitioning coefficient under equilibrium condition. In addition, SOM and black carbon (BC) present in soil may also influence the fate and transport of the POPs (Semple et al., 2013).

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In particular, BC is an essential kind of carbonaceous geo-sorbent (Accardi-Dey and Gschwend, 2002) that influences the general conduct of organic contaminants in soils due to porous nature and high adsorptive capacity (Sun et al., 2008). Incomplete burning of fossil fuels and biomass generates BC (Ni et al., 2014). Although, BC is delivered near the burning of fossil fuels/biomass, yet they can fly out several thousand kilometers away from emission source. Organic carbon which are firmly tied with BC particles may also travel long distance away from emission source thereby limiting their bioavailability (Jonker and Koelmans, 2002; Huang et al., 2003; Ahrens and Depree, 2004; Koelmans et al., 2006).

Regardless of limited historical use of PCBs, elevated level of PCBs have been sometimes detailed in developing countries at lower latitudes (Breivik et al., 2011). Cities and urban centers are identified as significant sources of PCBs (Iwata et al., 1993; Harner et al., 2004; Jaward et al., 2004). Nepal is not a PCB manufacturing country; however, recently high level of atmospheric PCBs has been reported in urban areas (Yadav et al., 2017), and abundance of PCBs were connected to highly urbanized and industrial areas, demonstrating the potential source of release. Nepal is party to Stockholm Convention on POPs and has signed and ratified the convention in 2002 and 2007, respectively. The Stockholm Convention asks for the signatory nations to assess the viability of the Convention by performing long term monitoring of POPs in environmental matrices. Considering the significance of monitoring these semi-volatile organic compounds (SVOC) all through the world and of giving data on their dispersions between various ecological compartments, it is critical to measure the occurrence and distributions of these pollutants in Nepalese environment where very limited information on SVOC is available. Hence, the objective of this study is to measure the occurrence, profile and spatial distributions of PCBs in four noteworthy areas of Nepal with particular emphasis on air-soil exchange and soil-air partitioning. The role of TOC and BC was also studied to understand the fate and transport of PCBs.

2. Materials and methods

Details materials and methods are presented in [Supplementary Information](#).

2.1. Study area and sampling

Four major cities (Kathmandu, Pokhara, Birgunj, and Biratnagar) were chosen for collection of surface soil samples (Fig. S1). It covers an area of 642 km² with population about of 2.5 million (CBS/NPCS, 2011). Pokhara is the second largest city of Nepal with area 225 km², and population of about 0.32 million. Birgunj is a sub-metropolitan city covering an area of 22 km² with population of about 0.21million. It located in South-Central of Nepal near Indian border so called gateway to Nepal. Biratnagar is another sub-metropolitan city with an area of 59 km² and a population of about 0.24 million (CBS/NPCS, 2011). It is also known as the industrial capital of Nepal. A total of 72 surface soil samples were collected during August-October 2014 and combined to 24 representative samples covering all the four cities. Hence, each sample is representative of at least 3 sub samples collected at distance 5 m in different direction. The sampling locations and their typical description are described SI (Table S1). All the samples were packed in zipper bag after wrapping in aluminum foil and transported to laboratory keeping in ice box for further processing.

2.2. TOC and BC analysis

About 2–3 g of dried and sieved soil samples were treated with 3 mL of HCl (3%) and kept for 8 h. Then, the samples were washed thrice with de-ionized water and oven dried at 45 °C. A small portion of dried soil was used for TOC analysis by Elemental Carbon-Hydrogen-Nitrogen Analyzer (Elementar VARIO EL III). BC in soil samples was estimated

following chemo-thermal oxidation (CTO-375) technique described somewhere else (Elmquist et al., 2008; Gustafsson et al., 2001). Briefly, 2–3 g of soil samples was burnt in muffle furnace at 375 °C for 18 h under constant air flow. The burnt soil was then treated with 3 mL HCl (1 N), washed thrice with Milli-Q water and analyzed by Elemental CHN analyzer.

2.3. Extraction and analysis

About 20 g of dried and sieved soil was soxhlet extracted with 300 mL of DCM for 24 h. A known amount (20 ng) of mixture of tetrachloro-m-xylene; TCmX, PCB 30, PCB 198 and PCB 209 was added as surrogate standard. A small granule of copper was added to extracting flask to remove the elemental sulfur. The extracted samples were concentrated to 2–3 mL by rotary evaporation and subjected to column cleanup. About 3 cm of 3% deactivated neutral alumina, 3 cm of 3% deactivated neutral silica, 50% acid silica and 1 cm anhydrous sodium sulfate were packed in column from bottom to top, respectively. The extractant was eluted with 30 mL mixture of DCM and hexane (1:1 vol) and reduced to 0.2 mL under gentle nitrogen flow. A known amount (10 ng) of ¹³C-PCB-141 was added as internal standard prior to GC-MS analysis.

The eluted samples were injected into an Agilent 7890 A GC coupled with an Agilent 7000 A GC/MS Triple quadrupole with a CP-Sil 8CB capillary column (50 m × 0.25 mm × 0.25 μm) in EI mode and analyzed for thirty-two PCB congeners, specifically PCB-8,-28,-37,-44,-49,-52,-60,-66,-70,-74,-77,-82,-87,-99,-101,-105,-114,-118,-126,-128,-138,-153,-156,-158,-166,-169,-170,-179,-180,-183,-187, and -189. The GC-MS temperature program and injection time are explained somewhere else (Yadav et al., 2016). Briefly, 1 μL sample was injected in splitless mode and the injector temperature was 295 °C. The initial oven temperature was set at 60 °C for 1 min and raised to 220 °C at the rate of 30 °C/min (held for 0 min), then to 300 °C at the rate of 5 °C/min (held for 15 min) for PCBs. Helium was used as the carrier gas at a flow of 1 mL/min. The temperature of transfer line and ion source was maintained at 280 °C and 230 °C, respectively.

2.4. QA/QC

A complete set of calibration standards were injected to GC after every ten samples analyzed to check the cross contamination and interference. Ten procedural blank samples were tested in the similar way as original sample. The method detection limits (MDLs) of PCBs was 3 times standard deviation of all the blank samples. In case of non-detection of PCB chemical in blank, the MDL was calculated as 3 times S/N ratio obtained from lowest spiked standard. The MDL ranged from 0.4 to 1.1 pg/g for PCBs. The surrogate recoveries for TCmX, PCB 30, PCB 198 and PCB 209 in all soil samples vary from 88% to 110%, 91–119%, 89–105% and 95–121%, respectively. Out of 32 targeted congeners, only 30 congeners could be identified. PCBs concentrations were expressed on dry weight (dw) basis and were blank corrected but not corrected for recoveries.

2.5. Statistical analysis

Descriptive statistics, box-and-whisker plots, scattered plots and Spearman's rank correlation coefficient were analyzed and processed through IBM SPSS statistics (version 21). The Arc GIS (Version 9.3) was used to make spatial distribution maps. The non-detectable concentration of individual sample was set as zero for estimation and analysis.

Table 1
Descriptive statistics of PCBs in surface soil (ng/g).

PCBs Comps	Kathmandu				Pokhara				Birgunj				Biratnagar			
	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD
PCB8	0.28	0.51	0.35	0.09	0.25	0.32	0.28	nd	0.22	1.04	0.39	0.32	0.22	0.33	0.26	0.04
PCB28	0.54	1.54	0.90	0.42	0.49	1.18	0.75	0.23	0.40	9.18	2.01	3.52	0.50	0.77	0.61	0.12
PCB52	0.16	0.91	0.42	0.29	0.18	0.31	0.26	0.06	0.17	1.11	0.36	0.37	0.19	0.34	0.23	0.06
PCB49	0.40	1.03	0.62	0.25	0.28	0.63	0.45	0.14	0.25	2.16	0.69	0.73	0.42	0.91	0.53	0.19
PCB44	0.14	0.66	0.27	0.20	0.13	0.23	0.16	0.05	0.14	0.93	0.30	0.31	0.14	0.18	0.16	0.02
PCB37	0.63	1.91	1.01	0.49	0.63	1.03	0.74	0.15	0.59	5.46	1.45	1.97	0.62	0.72	0.66	0.04
PCB74	0.67	0.92	0.75	0.11	0.65	0.85	0.70	0.08	0.64	1.76	0.87	0.44	0.66	0.70	0.68	0.02
PCB70	0.39	0.98	0.59	0.23	0.36	0.72	0.45	0.13	0.33	3.84	1.05	1.39	0.35	0.47	0.41	0.04
PCB60	0.44	1.22	0.65	0.31	0.42	0.73	0.51	0.12	0.42	3.28	0.94	1.15	0.42	0.50	0.46	0.03
PCB101	nd	1.34	0.34	0.51	nd	0.20	0.10	0.07	nd	0.46	0.19	0.19	nd	0.17	0.10	0.07
PCB99	0.32	0.88	0.47	0.22	0.32	0.40	0.35	nd	0.32	0.64	0.42	0.14	0.32	0.35	0.33	0.02
PCB87	0.17	0.78	0.34	0.23	0.18	0.25	0.22	nd	0.18	0.42	0.26	0.10	0.18	0.23	0.20	0.02
PCB77	0.76	1.32	0.93	0.22	0.76	0.95	0.82	0.07	0.76	1.50	0.91	0.29	0.76	0.83	0.79	0.03
PCB82	0.12	0.37	0.20	0.10	0.11	0.19	0.15	nd	0.11	0.19	0.14	0.03	0.12	0.14	0.13	0.01
PCB114	0.23	0.29	0.26	0.02	0.24	0.31	0.27	nd	0.23	0.25	0.24	0.01	0.23	0.27	0.25	0.01
PCB153	0.27	4.60	1.63	1.76	0.24	1.66	0.55	0.55	0.23	1.42	0.56	0.44	0.25	1.76	0.63	0.57
PCB105	0.51	1.33	0.72	0.32	0.51	0.67	0.56	0.06	0.51	1.24	0.75	0.35	0.51	0.64	0.55	0.05
PCB179	0.27	0.60	0.38	0.13	0.27	0.38	0.30	0.04	0.27	0.34	0.29	0.03	0.27	0.44	0.31	0.06
PCB158	0.47	5.28	2.07	1.92	0.38	2.27	0.93	0.75	0.37	2.88	1.07	0.94	0.40	2.50	0.84	0.82
PCB138	nd	0.37	0.14	0.13	nd	0.26	0.10	0.09	nd	0.26	0.10	0.08	nd	0.18	0.10	0.05
PCB126	0.73	0.93	0.80	0.09	0.74	0.92	0.81	0.08	0.74	0.79	0.75	0.02	0.74	0.79	0.77	0.02
PCB166	0.24	0.28	0.25	0.02	0.23	0.29	0.24	nd	0.23	0.25	0.24	0.01	0.23	0.24	0.23	0.00
PCB187	0.14	1.54	0.65	0.61	0.14	0.77	0.29	0.24	0.14	0.45	0.23	0.12	0.15	1.03	0.32	0.35
PCB183	nd	0.74	0.23	0.26	nd	0.39	0.11	0.14	nd	0.28	0.10	0.09	0.06	0.35	0.14	0.11
PCB128	0.10	0.88	0.35	0.31	nd	0.20	0.14	0.05	nd	0.56	0.21	0.17	0.10	0.52	0.18	0.17
PCB156	0.49	0.91	0.68	0.20	0.50	0.59	0.54	0.04	0.49	0.60	0.54	0.05	0.49	0.71	0.54	0.08
PCB180	0.38	3.75	1.53	1.41	0.31	1.54	0.61	0.47	0.30	0.88	0.52	0.24	0.30	2.07	0.70	0.69
PCB169	1.17	1.28	1.20	0.04	1.17	1.28	1.21	nd	1.16	1.19	1.17	0.01	1.15	1.18	1.17	0.01
PCB170	0.21	1.93	0.82	0.76	0.18	1.05	0.41	0.33	0.21	0.56	0.32	0.15	0.27	1.25	0.47	0.38
PCB189	0.54	0.96	0.65	0.16	0.54	0.72	0.61	0.06	0.56	0.60	0.58	0.01	0.54	0.61	0.58	0.02
Σ ₃₀ PCBs	10.9	40.1	20.2	11.8	10.4	21.3	13.58	4.22	10.2	44.5	17.7	13.7	10.6	21.2	13.3	4.10
Σ ₇ DL-PCBs	4.44	7.03	5.24	1.05	4.47	5.44	4.81	0.39	4.45	6.17	4.96	0.74	4.43	5.03	4.65	0.23

nd: not detected.

3. Results and discussions

3.1. General comments on PCB concentration

Results of individual PCB congeners and Σ₃₀PCBs analyzed in soil samples are given in Table 1. Overall, the concentration of Σ₃₀ PCBs ranged from 10 to 59.4 ng/g dw (mean 12.2 ng/g ± 11.2 ng/g dw). PCB-158, -169 and -180 were the highly detected congeners among heavier congeners (with low vapor pressure), while PCB-28, -37 and -49 were the most detected among lighter congeners (with higher vapor pressure). The Σhexa-CBs and Σtetra-CBs were most abundant congeners followed by Σhepta-CBs, Σpenta-CBs and Σtri-CBs and accounted 27%, 25%, 17%, 16% and 13% on average, of ΣPCBs respectively. Site-wide individual concentration of PCBs has been shown in Fig. S2. Generally, the level of high-chlorinated PCBs (PCB-153, -158, -169 and -180) measured doubled time higher than low-chlorinated PCB (Fig. S2 and S3). This indicates the heavier PCB congeners are more likely retained in soil in tropical region (Devi et al., 2014; Chakraborty et al., 2016). However, the profile of ΣPCBs measured at BRS5 in Birgunj showed significantly different pattern than rest of the samples, were tri and tetra-CBs were most dominant followed by hexa- and penta-CBs and accounted 37%, 37%, 9% and 9%, of ΣPCBs, respectively. The PCB-28 and -37 was most contributing individual PCB among tri-CBs, while PCB-70 and -60 offered elevated level of tetra-CBs in soil. This point toward fresh use of PCB (Chakraborty et al., 2016). BRS5 was located close proximity to petrol pump station, repairing workshop of motorcycle/car, and sales/showroom of different diesel and petrol engines. Further, government power house office for supplying electricity in the city is located in this area which might also release sufficient concentration of PCB from transformer oil.

3.2. Compositional profile and spatial distribution

The concentrations of individual PCB chemical analyzed in soil in this study have been specified in Table 1. Slightly higher concentration of ΣPCBs was detected in soil from Kathmandu and Birgunj than those of Pokhara and Biratnagar. The concentrations of ΣPCBs ranged from 10.9 to 40 ng/g dw (mean 20.2 ± 11.8 ng/g dw), 10.1–44.5 ng/g dw (mean 17.6 ± 13.6 ng/g dw), 10.4–21.3 ng/g dw (mean 13.6 ± 4.20 ng/g dw), and 10.6–21.2 ng/g dw (mean 13.3 ± 4.10 ng/g dw) in Kathmandu, Birgunj, Pokhara and Biratnagar, respectively (Fig. 1). The concentration of ΣPCBs measured in this study was compared with previous studies around the world (Table S2). It is interesting to note that the level of ΣPCBs measured in this study was about doubled times lower than those observed in Glasgow, Scotland (22 ng/g) (Cachada et al., 2009) and Cedar Rapids, USA (3–1200 ng/g) (Martinez et al., 2012). This indicates relatively less contamination of Nepalese soil by PCBs than Scotland and USA. However, the levels of PCBs were slightly higher than those detected in soil samples from Istanbul, Turkey (1.5–9.5 ng/g) (Cetin et al., 2017), Bahia Blanca, Argentina (0.3–1.7 ng/g) (Tombesi et al., 2017), Moscow, Russia (5–31 ng/g) (Wilcke et al., 2006), and Hong Kong, China (1.6–9.8 ng/g) (Zhang et al., 2007a, b). In addition, the PCBs level in this study was comparable with those observed in Aveiro, Portugal, Uppsala, Sweden, Ljubljana, Slovenia and Torino (Italy) (Cachada et al., 2009)(Table S2).

The major sources of PCBs in urban area are known to release from dielectric fluid, electrical transformers and hydraulic fluid contamination (Yadav et al., 2017; Aichner et al., 2007). Low molecular weight PCBs are mainly used in transformers, capacitors and lubricants, while those with higher molecular weight are applied in paint and plasticizers (Wu et al., 2011). Moreover, blasting of wastes comprising PCBs and inappropriate destroying of e-waste for profitable metal reuse through

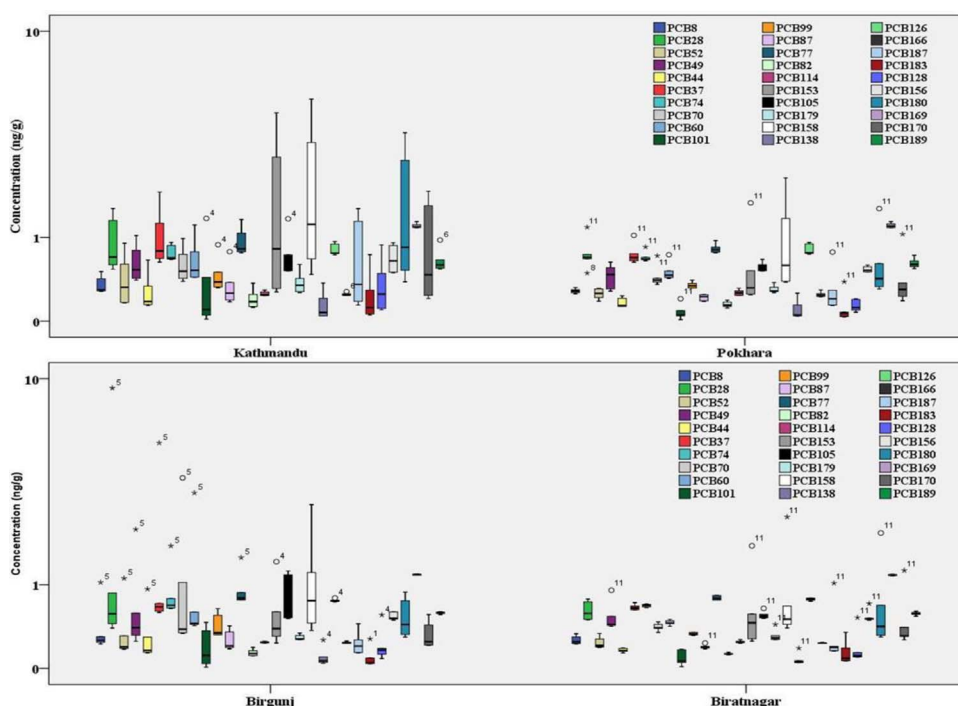


Fig. 1. Boxplot showing levels of individual PCB in Nepalese soil. The concentration in Y-axis is logarithmic scale.

open blazing and corrosive wash could not be neglected as emerging source of PCBs discharge (Gioia et al., 2014; Sun et al., 2016). Nepal is not a PCBs delivering nation, and being a developing country there is no such PCB utilizing industries are accessible (NIP, 2007). However, substantial amount of PCBs was imported through various donor countries for setting up the hydropower (HP) project in Nepal. Also, the import of large quantities of dielectric fluid and transformer oil for electrification in Nepal could be the possible entry of PCBs (NIP, 2007). It is estimated that more than 2000 pieces of metering units each containing about 150 l of dielectric fluid together with about 20,000–25,000 welding machines each containing about 40 l of dielectric fluid are in current use throughout the country (NIP, 2007). PCBs are used in transformer oil. The principal PCB homologue of oil constitutes tri-CBs, tetra-CBs, and di-CB accounting 63%, 24% and 9%, respectively (Ren et al., 2007). The predominance of tetra- and tri-CBs in this study suggests possible source of PCBs from transformer oil, while abundance of hexa-, penta- and hepta-CBs indicated use of PCBs in Nepalese products such as lubricants, breaker oil, cutting oil and paints, and cable insulation (NIP, 2007; Ren et al., 2007). The homologue patterns of PCBs showed that the real pattern in one city different from another. Hexa-CBs were the major homologues measured in Kathmandu, Pokhara and Biratnagar while tetra-CBs dominated in Birgunj's soil. However, PCBs homologues patterns of one city with another were statistically non-significant. Similar pattern of PCB homologues has been reported previously (Kang et al., 2000; Ren et al., 2007).

In this study, the PCB homologues measured in the surface soil are shown in Fig. 2. The major PCB homologues in all four cities were controlled by hexa-CBs (22–31%) followed by tetra-CBs (20–29%), hepta-CBs (12–21%), penta-CBs (15–17%) and tri-CBs (9–19%), respectively (Fig. 2 and S4). This might be due to fact that the heavier PCBs are deposited nearer the source whereas lighter one gets transported over longer distance after their release from source materials (Ren et al., 2007). The PCB homologues pattern observed in this study is consistent with previous reports from Kenya and informal e-waste recycling sites of China (Wang et al., 2011; Sun et al., 2016). The top three homologues (hexa-, tetra- and hepta-CBs) measured in surface soil in this study were slightly different to those measured in global background soil (Meijer et al., 2003). The principal homologue profile of the

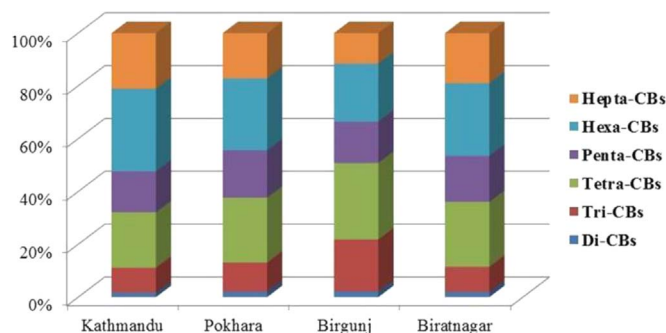


Fig. 2. Profile of PCB-homologues showing mean % contribution of target PCBs to ΣPCBs.

global PCB production constitutes tri-, tetra- and penta-CBs (Breivik et al., 2002). The compositions of tri-, tetra- and penta-CB homologues were also high in this study indicating higher PCBs in Nepalese product. However, Aichner et al. (2007) didn't find any distinct pattern among PCBs homologues analyzed in surface soil from Kathmandu and suggested background contamination of ubiquitous PCBs.

The spatial distribution map of PCBs measured in soil samples has been shown in Fig. 3. Extremely high concentration of ΣPCBs was measured at KTS 4 in Kathmandu and BRS 5 in Birgunj (Fig. 3 and Fig. S5). High levels of ΣPCBs were also detected at KTS 5 and KTS 6 in Kathmandu, PKS 5 in Pokhara, BRS4 in Birgunj and BTS5 in Biratnagar, respectively (Fig. 3 and Fig. S5). The elevated levels of PCBs were related to roadside soil with heavy traffic, urban -residential, -commercial and -industrial area. The least concentration of ΣPCBs was measured at BRS2, BRS6 in Birgunj and PKS2 in Pokhara, respectively.

The Global Environmental Monitoring System has distinguished the seven indicator PCBs (PCB-28,-52,-101,-118,-138,-153, and -180) as significant food contaminants (WHO, 2004), in the light of fact that they are pervasively present in various environmental matrices, and record for over half of the aggregate non-dioxin-like PCBs (EFSA, 2005; Liu et al., 2011). The total concentration of 6 indicator PCBs (PCB-28,-52,-101,-138,-153, and -180) in this study ranged from 1.5 to 12.4 ng/g dw, 1.1–11.9 ng/g dw, 1.33–5.02 ng/g dw and 1.36– 5.22 ng/g dw in Kathmandu, Birgunj, Pokhara and Biratnagar, respectively. Like total PCBs, the indicators PCBs were also highly detected in Kathmandu and

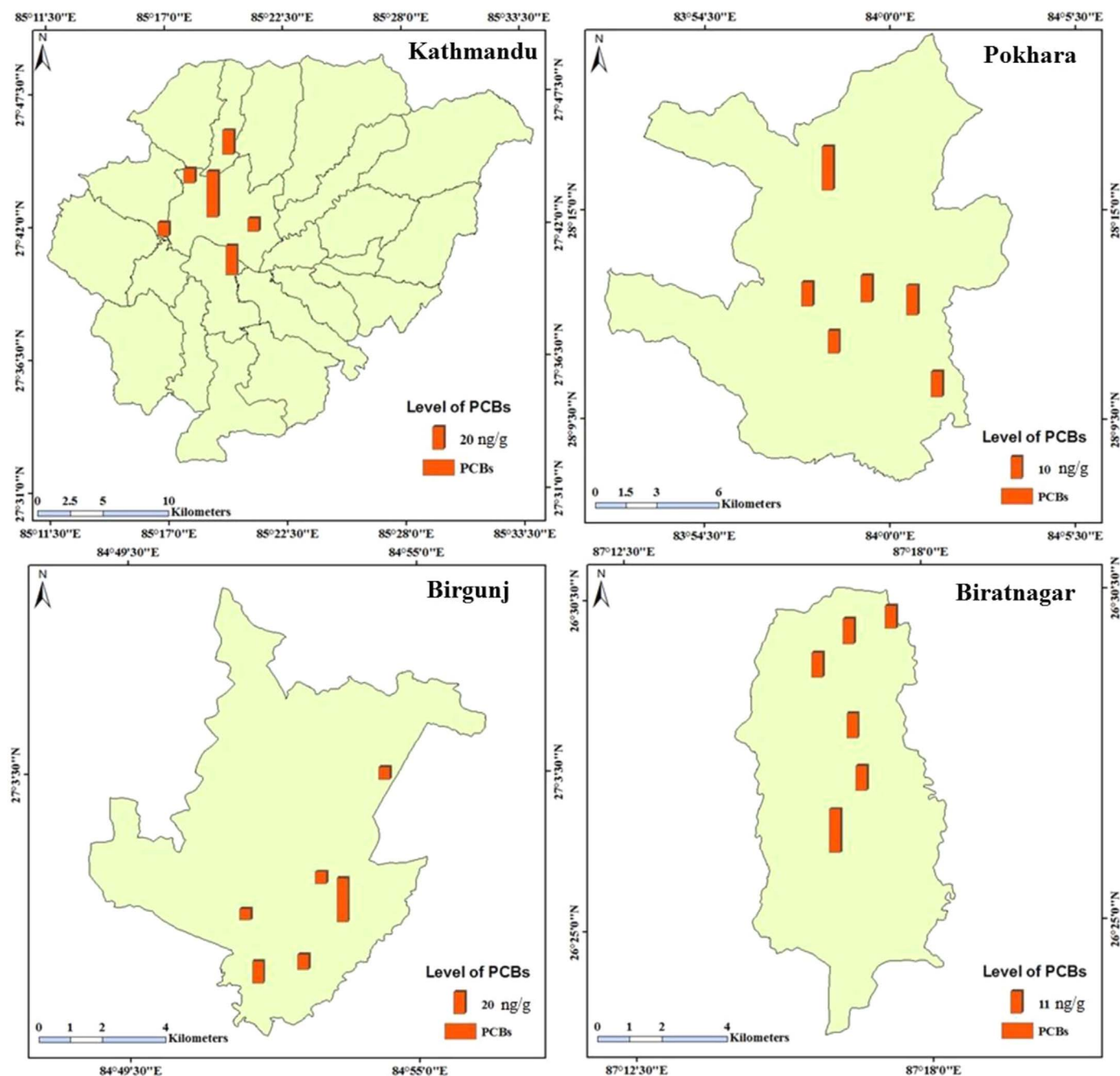


Fig. 3. Spatial distribution of PCBs in surface soil of Nepalese cities (ng/g).

Birgunj than Pokhara and Biratnagar. Kathmandu being the largest and capital city, while, Birgunj is the gateway to Nepal for most of its trade with India through open border might cause exceeding level of Σ PCB. The PCBs levels in these cities could be most probably from the past application of PCB- holding equipment. Also, the possible source of PCBs contamination might release from large number of old transformers pilled at repairing workshop of Nepal Electricity Authority (NEA), in Kathmandu (NIP, 2007).

The sum of 7 dioxin-like-PCBs (DL-PCBs) (PCB-77,-105,-126,-156,-169,-189, and -114) ranged from 4.4 to 7 ng/g dw (mean 5.24 ± 1.05 ng/g dw), 4.47–5.44 ng/g dw (mean 4.81 ± 0.39 ng/g dw), 4.45–6.17 ng/g dw (mean 4.96 ± 0.74 ng/g dw) and 4.4–5 ng/g dw (mean 4.65 ± 0.23 ng/g dw) in Kathmandu, Pokhara, Birgunj and Biratnagar, respectively. PCB-169 was the dominant PCB with highest concentration in all DL-PCBs followed by PCB-77 and -126 (Fig. S6). DL-PCBs constituted 26%, 35%, 28% and 35% of total PCBs in

Kathmandu, Pokhara, Birgunj and Biratnagar, respectively. The percentage/proportion of DL-PCBs constituents obtained in this study was much higher than those reported in soil samples from Istanbul (4–13%) (Kuzu et al., 2016) and Turkey (15%) (Yolsal et al., 2014). However, the DL-PCBs constituent in this study was consistent with previous study reported in urban area of Pakistan, where DL-PCBs accounted 35% of total PCB in soil (Syed et al., 2013).

3.3. Effect of TOC and BC

The soil organic matter (SOM) and black carbon (BC) is essential parameters that significantly influence soil–air exchange process and atmospheric long-range transport of organic pollutants because of their higher sorption capacity (Walker et al., 1999; Cabrerizo et al., 2011; Degrendele et al., 2016). SOM represents 1.5 times of total organic carbon (TOC). Generally, the TOC content in soil samples in this study

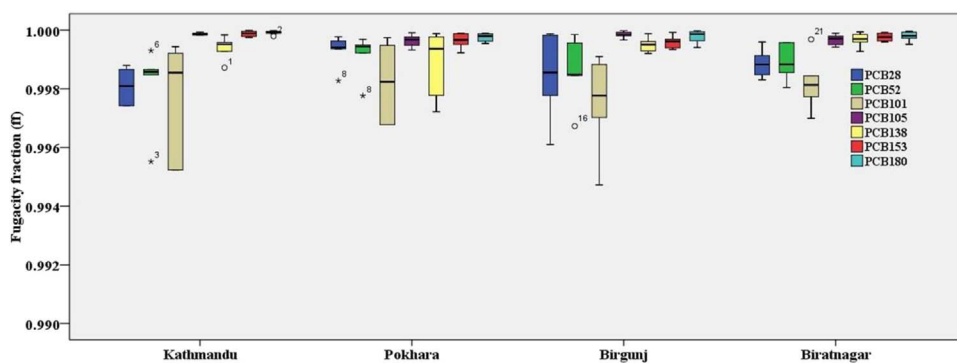


Fig. 4. Box and whisker-plot showing fugacity fraction of seven PCB congeners in Kathmandu, Pokhara, Birgunj and Biratnagar.

was less detected and ranged from 0.09% to 2.47% (mean $1.11 \pm 0.78\%$). A Spearman's rank correlation coefficient analysis was performed to investigate the relationship between PCBs and TOC. The results of the Spearman's rank correlation analysis are presented in Table S3. TOC content in soil was moderately and positively related to both high chlorinated CB-congeners (such as penta-, hexa- and hepta-CBs) ($Rho = 0.560, 0.472, \text{ and } 0.428, p < 0.01$) as well as less chlorinated CB-congeners (di-, tri- and tetra-CBs) ($Rho = 0.360, 0.474, \text{ and } 0.398, p < 0.01$), respectively. These results indicate that TOC is more or less important variable that control the distribution of PCBs in soil.

Although, BC constitutes only 4% of TOC in soil, it is considered a 'super-sorbent' because of its higher sorption capacity (Cornelissen et al., 2005; Nam et al., 2008). Its sorption ability is 10–100 times higher than amorphous organic matter (AOM) and is recognized to be in-charge of significant part of sorption/partitioning of POPs (Gustafsson and Gschwend, 1998; Nam et al., 2008). The concentration of BC quantified in soil samples was low and ranged from 0.025% to 0.586% (mean $0.173 \pm 0.179\%$). The Spearman's rank correlation showed that the PCB homologues were either moderately or weakly and positively correlated with BC content in soil. Penta-, tri-, tetra- and hepta-CBs were moderately correlated with BC ($Rho = 0.244, 0.221, 0.190 \text{ and } 0.186, p < 0.05$), respectively, however, deca- and hexa-CBs were weakly correlated with BC (Table S3). The low content of BC in soil together with more or less moderate association with homologue PCBs showed PCBs have less connection with BC. This indicates sorption by AOM (expressed in terms of TOC) not only but also BC is responsible for controlling PCB concentration in soil. Nonetheless, slightly high correlation coefficient of PCBs with TOC than BC demonstrated AOM plays more or less a significant role in retaining of PCBs in Nepalese soil than BC (Nam et al., 2008). This finding is in accordance with similar previous studies (Ghosh et al., 1999; Lohmann et al., 2005; Nam et al., 2008; Degrendele et al., 2016).

The ratios of BC/TOC are being broadly utilized to investigate the sources of BC (Muri et al., 2002a, b; Liu et al., 2011; Ali et al., 2015). In view of comparable contamination source in nature, past reviews proposed that BC/TOC proportion $\leq 11\%$ shows biomass burning, while BC/TOC proportion $\approx 50\%$ indicates outflow from fossil fuel source (Muri et al., 2002a, b; Oen et al., 2006; He and Zhang, 2009). In this study, the BC/TOC ratio in this study ranged from 1% to 15% (mean 4.16%) (Fig. S7). The BC/TOC ratio obtained in this study was lower than those reported in urban areas of Nanjing China (mean 29%) (He and Zhang, 2009), Norway (6.4–12.3%) (Oen et al., 2006), USA (16–18%) (Accardi-Dey and Gschwend, 2002), Brazil (2.3–12.8%) (Ribeiro et al., 2008) and Spain (3–16.5%) (González-Vila et al., 2009). The average BC/TOC ratio estimated was below 6%, suggesting emission from biomass burning and atmospheric deposition is the major source of BC. However, slightly high % of BC/TOC at KTS1 (11%), and BRS 2 (15%) suggest prevalence of anthropogenic sources of BC pollution compared to atmospheric deposition and biomass burning.

3.4. Air-soil exchange of PCBs

The fugacity fractions of individual PCB congeners were calculated to define the trend of air-soil exchange. The SOM represent the fugacity ability of soils (Mackay, 2001), whereas fugacity of air is basically identified as atmospheric concentration. In this study, air fugacity was calculated utilizing atmospheric concentration of PCBs obtained from passive sampling of each cities (Yadav et al., 2017), while soil fugacity was estimated based on SOM present in surface soil. Fugacity fractions (ff) are more commonly utilized to trace the bearing of soil-air exchange (Mackay, 2001; Cabreriezo et al., 2011; Aliyeva et al., 2012; Devi et al., 2014; Degrendele et al., 2016). Mathematically, it can be expressed as:

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

Where, f_s and f_A are the soil and air fugacity, respectively. The f_s and f_A can be further calculated by following equations (Cabreriezo 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 and C_s are the air concentration (ng/m^3) and soil concentration (ng/g) of individuals PCBs, respectively. R is universal gas constant ($8.314 \text{ Pa m}^3/\text{mol}/\text{K}$), T is the average absolute temperature (K), ϕ_{OM} is the fraction of soil organic matter (which is 1.5 times of TOC), K_{OA} is the octanol air partition coefficient and obtained from Mackay et al. (2006), and 0.411 is correlation coefficient constant between K_{SA} and K_{OA} . Theoretically, $ff = 0.5$ indicate equilibrium, $ff > 0.5$ indicates volatilization and net emission into the air and $ff < 0.5$ indicate deposition and net transport from the air to soil. However, Harner et al. (2001) studied the uncertainty or potential error in ff and suggested $ff > 0.7$ for net volatilization (Harner et al., 2001). Fig. 4 and Table S4 provide the ff of PCBs in all four cities. It is evident from Fig. 4 that the ratio of soil to air fugacity (ff) at all study sites was either 1 or close to 1, strongly indicating the soil serves as the sources of PCBs. This finding is consistent with previous studies from Azerbaijan (Aliyeva et al., 2012), UK (Cabreriezo et al., 2011), and some European countries (Degrendele et al., 2016).

3.5. Soil-air partition coefficient

The soil-air partitioning coefficient was calculated by measuring the concentration of PCBs in soil and air. The atmospheric concentrations of PCBs in this study were acquired from Yadav et al. (2017) for calculation purpose. The soil-air partitioning coefficient K_{SA} (L/Kg) can be calculated as (Cabreriezo et al., 2009):

$$K_{SA} = 1.10^9 C_s / C_A \quad (4)$$

Where, C_s is the concentrations of individual PCBs in soil (ng/g), and C_A is the concentration of individual PCBs in air (pg/m^3).

The TOC and BC dependent K_{SA} was further predicted by absorption model developed by Finizio et al. (1997) and later modified by Ribes

et al. (2003). The model assumes that absorption into the soil organic matter is the main process responsible for soil-air partitioning and can be expressed mathematically as follows (Ribes et al., 2003): -

$$K_{SA} = 1.5 \left(\frac{f_{TOC}}{\delta_{OCT}} \right) K_{OA} \tag{5}$$

Where, f_{TOC} denotes the fraction of total organic carbon (g/g dw), δ_{OCT} is the octanol density (0.820 kg/L at 20 °C), and K_{OA} represents octanol-air partition coefficient. The K_{BC-A} model estimate the role of black carbon in the adsorption of PCBs (Ribes et al., 2003).

$$K_{SA} = 1.5 \left(\frac{f_{TOC}}{\delta_{OCT}} \right) K_{OA} + f_{BC} K_{BC-A} \tag{6}$$

Where, f_{BC} is the fraction of BC (g/g dw) in soil, and K_{BC-A} is the black carbon air partition coefficient and can be estimated as follows (Ribes et al., 2003): -

$$\text{Log} K_{BC-A} = -0.85 \text{Log} P_L + 8.94 - \text{Log} \left(\frac{998}{AEC} \right) \tag{7}$$

A_{EC} is the specific surface area of BC which is 100 m²/g (Dachs et al., 2004; Prevedouros et al., 2008).

The octanol-air partition coefficient and black carbon-partition coefficient of PCBs compounds were obtained from literature and are presented in Table S5. The temperature dependent K_{OA} and K_{BC-A} were studied as predictor of K_{SA} (Fig. 5). Good association were observed between measured $\text{Log} K_{SA}$ and $\text{Log} K_{OA}$ ($R^2 = 0.483$). Measured $\text{Log} K_{SA}$ was also positively and linearly correlated with $\text{Log} K_{BC-A}$ ($R^2 =$

0.438). This indicates the octanol is suitable surrogate for soil organic matter. Further, Slightly weak but positive correlation of measured $\text{Log} K_{SA}$ with $\text{Log} K_{OA}$ ($R^2 = 0.483$) and $\text{Log} K_{BC-A}$ ($R^2 = 0.438$) suggests that both $\text{Log} K_{OA}$ and $\text{Log} K_{BC-A}$ can predict soil-air partitioning for PCBs to lesser extent. The correlation coefficient of $\text{Log} K_{SA}$ and $\text{Log} K_{OA}$ ($R^2 = 0.483$) observed in this study was comparable with previous studies from urban sites in Serbia ($R^2 = 0.70$) and around the world (Finizio et al., 1997; Meijer et al., 2003; Radonic et al., 2011).

Soil-air partitioning coefficient is crucial parameter for modelling the fate of POPs in the environment. We compared the measured K_{SA} from Eq. (4) with those predicted by absorption model developed by Finizio from Eqs. (5) and (6). Good agreement ($R^2 = 0.606$) was observed between measured and predicted K_{SA} from K_{OA} (Fig. 5). Good linear correlation between K_{SA} and K_{BC-A} was also found with slightly lower R^2 (0.546) value than K_{OA} . Since this model assumes that absorption by soil organic matter is the main sorption process responsible for soil-air partitioning at soil-air interface, the possibility of adsorption process was not considered. Hence, present study suggests the absorption by soil organic matter control soil-air partitioning for PCBs. Similar finding was reported earlier in Central Europe by Degrendele et al. (2016).

4. Conclusions

The concentration of PCBs in surface soil was investigated from four major cities of Nepal with special interest on soil air exchange and the soil-air partitioning phenomenon. Generally, high chlorinated PCB congeners were twice as high as less chlorinated congeners. The most

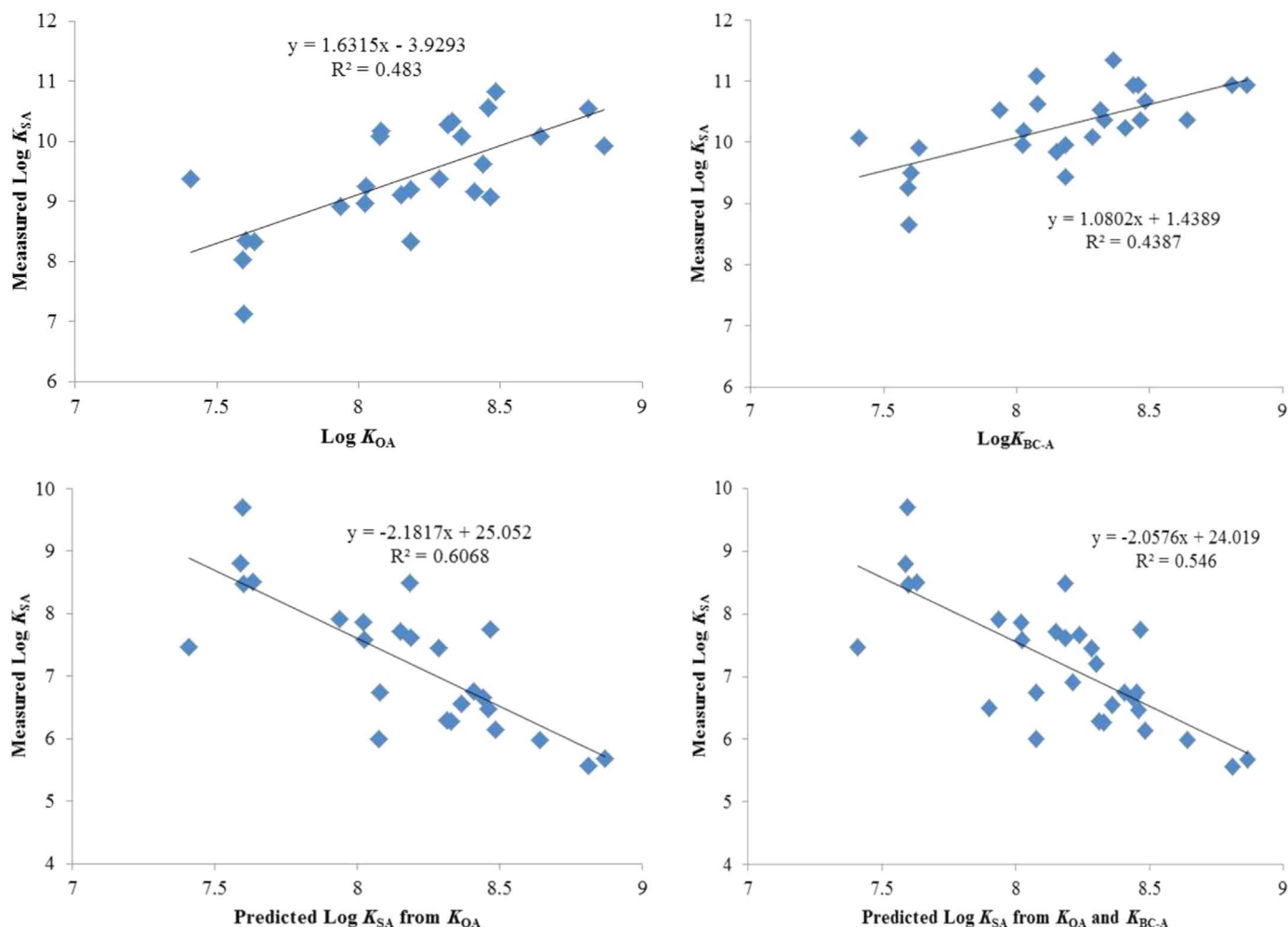


Fig. 5. Influence of $\text{Log} K_{OA}$ and $\text{Log} K_{BC-A}$ on measured $\text{Log} K_{SA}$ (top) and comparison of measured and predicted K_{SA} (bottom).

significant sources of PCBs in Nepalese soil were identified as emission from transformer oil, lubricants, breaker oils, paints, and cable insulation. Slightly high correlation of PCBs with TOC than BC demonstrated that TOC is important variable that control the distribution of PCBs in soil. The ratio of soil to air fugacity (f/f) results showed that the soil control the atmospheric level of banned PCB in Nepal through deposition and net transport. The soil-air partitioning coefficient study suggests the absorption by soil organic matter control soil-air partitioning for PCBs.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.ecoenv.2017.06.057>.

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