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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 ± 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 $K_{BC\text{-}A}$ (R^2 = 0.438) suggests that both Log K_{OA} and Log $K_{BC\text{-}A}$ 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 km^2 with population about of 2.5 million (CBS/NPCS, 2011). Pokhara is the second largest city of Nepal with area 225 km^2, and population of about 0.32 million. Birgunj is a sub-metropolitan city covering an area of 22 km^2 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 km^2 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 ^{13}C-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.