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
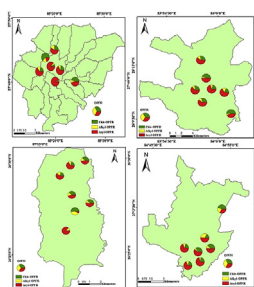
ABSTRACT

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

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