



# Occurrence and fate of organophosphate ester flame retardants and plasticizers in indoor air and dust of Nepal: Implication for human exposure<sup>☆</sup>



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## ABSTRACT

The present study was carried out in Nepal, a landlocked country located between world's two most populous countries i.e. India and China. In this study, the occurrence, profiles, spatial distributions and fate of eight organophosphate ester flame retardants (OPFRs) were investigated in indoor air and house dust. Overall, the concentrations of  $\sum$ OPFR were in the range of 153–12100 ng/g (median 732 ng/g) and 0.32–64 ng/m<sup>3</sup> (median 5.2 ng/m<sup>3</sup>) in house dust and indoor air, respectively. The sources of high OPFR in the indoor environment could be from locally used wide variety of consumer products and building materials in Nepalese houses. Significantly, high concentration of tri-cresyl phosphate (TMPP) was found both in air and dust, while tri (2-ethylhexyl) phosphate (TEHP) had the highest concentration in air samples. It might be due to fact that the high concentrations of TMPP are related to intense traffic and/or nearby airports. On the other hand, significantly high concentration of TEHP could be due to anthropogenic activities. Only TEHP showed positive correlation between indoor air and house dust ( $Rho = 0.517, p < 0.01$ ), while rest of compounds were either less correlated or not correlated at all. The estimated human exposure to  $\sum$ OPFR via different pathway of intake suggested dermal absorption via indoor dust as major pathway of human exposure to both children and adult population. However, other pathways of OPFR intake such as dietary or dermal absorption via soil may still be significant in case of Nepal.

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## 1. Introduction

Organophosphate ester flame retardants (OPFRs) are a group of man-made chemicals widely applied as flame-retardants (FRs), plasticizers, antifoaming agents, and additives in hydraulic fluids, lacquers, and floor polishes (Reemtsma et al., 2008). OPFRs can also be used as extractive solvents in hydrometallurgy and nuclear energy (Reemtsma et al., 2008). The biodegradability and bio-accumulation potential of OPFRs were studied in the 1970s for the first time and later during 1980s (Muir et al., 1985; Saeger et al., 1979; Sheldon and Hites, 1978). The studies were either abandoned during 1990s because most aryl and alkyl phosphate were degradable in the

environment or ignored due to higher production of brominated flame retardants. However, the interest in these chemicals re-emerged at the end of the 1990s after being reported in the indoor environment and wastewater treatment plant and due to increased production after polybrominated diphenyl ethers (PBDE) phase outs (Carlsson et al., 1997; Meyer and Bester, 2004). There is still, very limited information available about the occurrence and fate of OPFRs in many developing countries including Nepal.

The restriction and regulation of PBDEs resulted in the widespread application of OPFRs as alternate FRs (Stapleton et al., 2009; USEPA, 2005). Chlorinated alkyl phosphates such as tris-2-chloroethyl phosphate (TCEP), tri-(1-chloro-2-propyl) phosphate (TCIPP), and tris-1,3-dichloro-2-propyl phosphate (TDCIPP) are generally used as FRs in flexible and rigid polyurethane foams (Stapleton et al., 2009). The non-chlorinated alkyl phosphates, such as tri-ethyl phosphate (TEP), tri-*n*-butyl phosphate (TNBP), tri-*iso*-butyl phosphate (TIBP) are mostly applied as plasticizers in

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unsaturated polyester resins, cellulose acetate, polyvinylchloride, acrylonitrile-butadiene styrene, and synthetic rubber (Marklund et al., 2005a). Tri-phenyl phosphate (TPHP) and TMPP are generally employed as FRs and/or plasticizers in PVC, cellulosic polymers, thermoplastics, and synthetic rubber (EFRA, 2010a, b). In addition, TPHP is also utilized in polyurethane foams (Stapleton et al., 2009; WHO, 1990, 1991). Furthermore, TNBP, TPHP, and TMPP are also applied in hydraulic fluids as lubricants (Solbu et al., 2007).

Since OPFRs are not covalently bonded to the polymer matrix, they are easily released into the indoor and outdoor environment through abrasion and volatilization (Marklund et al., 2003; Wensing et al., 2005). The presence of OPFR globally has been observed in the hydrosphere (Bollmann et al., 2012; Regnery et al., 2011), atmosphere (Moller et al., 2012; Regnery and Püttmann, 2010; Salamova et al., 2014a), and biosphere (Shah et al., 2006; Sundkvist et al., 2010). In the marine environment, OPFR were also measured in seawater (Bollmann et al., 2012), biota (Sundkvist et al., 2010), and atmospheric particles (Castro-Jimenez et al., 2014; Lai et al., 2015; Moller et al., 2011; Salamova et al., 2014b). Most OPFRs, such as TCEP, TCIPP and TDCIPP, have a low degradation potential and thus may persist in surface and subsurface environment for a long time (Meyer and Bester, 2004; Reemtsma et al., 2008). When released into indoor environments by volatilization, they may undergo partitioning between the gas phase, organic films on surfaces, and airborne particulate matter (Weschler and Nazaroff, 2008). It is estimated that approximately 90% of the world's production of FRs (of which 20% are OPFRs), ends up in electronics and plastics, while only 10% applied to coated fabrics and upholstery furniture and bedding products (Hopes, 2010; IVF, 2009).

Information about contamination of OPFRs in different environmental matrices in developing Asian countries is scarce (Ali et al., 2013; Kim et al., 2013). To the best of our knowledge, very limited information is available on the levels, profiles, and spatial distribution of OPFRs in indoor air and house dust from whole of the Indian subcontinent in general and specifically in case of Nepal. Although Yadav et al. (2017a) measured high levels of brominated and chlorinated FRs in urban areas of Nepal, the environmental concentrations and fate of OPFRs have not been explored so far. Therefore, the objective of this study is to investigate the occurrence, spatial distribution, and fate of eight OPFRs in indoor air and house dust from Nepal, South Central Asia. Further, human exposure of OPFRs to Nepalese population via different pathway of intake was estimated. The data generated from this study could be useful for understanding the present status of OPFRs contamination in Nepal.

## 2. Material and methods

Detailed descriptions of the materials and methods are given in [Supporting Information](#) part.

### 2.1. Study area

Four major cities (Kathmandu, Pokhara, Birgunj, and Biratnagar) in Nepal were selected for collection of indoor air and dust samples (Fig. S1 and Table S1, [supporting information](#)). Indoor air (N = 34) and dust samples (N = 28) were collected from different environmental compartments during August–October 2014. The details about sampling locations of the study are presented elsewhere (Yadav et al., 2017b).

### 2.2. Air sampling

A total of 34 polyurethane foam passive air sampling (PUF-PAS) samplers (8 each at Pokhara, Birgunj, Biratnagar and 10 at Kathmandu) were deployed in different households of previously

selected cities. These households were located in residential, offices premises, public places, and near heavy traffic environments. After exposure, all PUF samples were retrieved, wrapped in aluminum foil and sealed in zipper bag. Then, the PUF were transported to the laboratory keeping in ice box, immediately through air mail and stored at  $-20^{\circ}\text{C}$  until analysis. The details about passive air sampling procedure for collection of air samples was described elsewhere (Liu et al., 2016).

### 2.3. Dust sampling

A total of 28 household dusts were collected from indoor environment representing domestic, occupational, and public environments. Samples were collected by sweeping of kitchen room, study room, bed room, living room, office and passage of the households. Dust samples were collected using vacuum cleaner made for domestic purpose. Separate paper dust bags were used to collect dust samples from individual household. About 50 g of dust samples were collected and packed in zipper bag before transporting them to wet chemistry laboratory at State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry. In the laboratory, the dust samples were homogenized, sieved with mesh size of 500  $\mu\text{m}$  and stored at  $-20^{\circ}\text{C}$  until analysis.

### 2.4. Sample preparation and extraction

PUF disks and dust samples were spiked with 5  $\mu\text{l}$  (200 ng/ $\mu\text{L}$ ) deuterated tris (2-chloroethyl) phosphate (TCEP-d12), as surrogate standard and were Soxhlet extracted with DCM for 24 h. Copper granules were added to the round bottle flask before extraction to remove the elemental Sulphur present dust sample. Copper granules were prewashed and activated with hydrochloric acid prior adding to flask. The sample extract was concentrated by rotary evaporator (Heildolph 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) (SPELCO, USA). Prior to fractionation, Florisil cartridges were prewashed 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  $\mu\text{l}$  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.

### 2.5. GC-MS analysis

OPFRs analysis was performed in an Agilent 7890A GC coupled with an Agilent 7000A GC/MS single quadrupole in EI mode. The detail about GC-MS parameter has been presented in [Table S2](#). Briefly, the temperature of transfer line and ion source was maintained at  $280^{\circ}\text{C}$  and  $230^{\circ}\text{C}$ , respectively. The GC oven temperature started at  $60^{\circ}\text{C}$  for 1 min, increased to  $220^{\circ}\text{C}$  at a rate of  $30^{\circ}\text{C min}^{-1}$  (held for 0 min), then to  $300^{\circ}\text{C}$  at a rate of  $5^{\circ}\text{C min}^{-1}$  (held for 15 min). Eight OPFRs such as TCEP, TDCIPP, TCIPPs (mix of three isomers), TNBP, TPHP, EHDPHP, TEHP and TMPP (mix of three isomers) were targeted. The full name and details of individual OPFRs is given in [Table S2](#).

### 2.6. QA/QC

Three field blank (only for air sample) and ten laboratory blank

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