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Concentrations, sources and health risk of nitrated- and oxygenated-polycyclic aromatic hydrocarbon in urban indoor air and dust from four cities of Nepal

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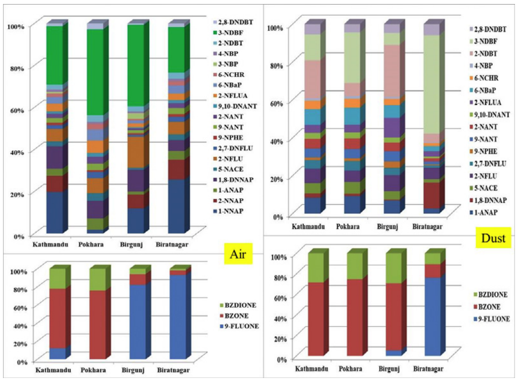
HIGHLIGHTS

- The $\sum_{19}$NPAHs in air and dust were 5 and 2 times lower than parent $\sum_{16}$PAHs, respectively.
- 3-nitrodibenzofuran was the most abundant measured both in air and dust
- 2-NFLUA/1-NPYR indicated contribution from secondary emission via photochemical reaction
- Dermal contact via dust was the primary route of NPAH/OPAHs exposure to Nepalese population.

GRAPHICAL ABSTRACT



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ABSTRACT

Although the fate and behavior of parent polycyclic aromatic hydrocarbon (PAHs) have been documented worldwide, the information about PAH-derivatives (NPAHs and OPAHs) is limited, especially in developing countries, including Nepal. Moreover, the greater parts of the investigations concentrating on NPAHs/OPAHs are on the air (borne) particulate phase only; and are primarily based on a limited number of compounds analyzed. Little is known about the environmental concentration, fate, and behavior of NPAHs and OPAHs in air gas phase and dust. In this study, the concentration, fate, spatial distributions of 26 NPAHs and 3 OPAHs in the air ($n = 34$) and dust ($n = 24$) were investigated in suspected source area/more densely populated areas of Nepal. Four critical source areas in Nepal were considered as it was conjectured that the urban areas are more prone to NPAH/OPAH contamination due to the high density of automobiles and industrial activities. Overall, the measured $\sum_{19}$NPAHs in air and dust were 5 and 2 times lower than their parent-PAHs, respectively. Highest levels of NPAHs/OPAHs were measured in Birgunj, followed by Kathmandu, Biratnagar, and Pokhara, respectively, while Biratnagar showed the highest level of $\sum$OPAHs. 3-Nitrodibenzofuran (3-NDBF) was the most abundant NPAHs measured both in air and dust, whereas 9-Fluorenone (9-FLUONE) prevailing OPAHs. The molecular diagnostic ratio (MDR) of 2-Nitrofluoranthene/1-Nitropyrene indicated the contribution from secondary emission via photochemical reaction as the primary source of NPAHs, while solid fuel combustion and crop residue burning were identified as the essential sources of OPAHs. The human exposure to NPAH/OPAH through the different

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route of intake suggested dermal contact via dust as the primary pathway of NPAH/OPAH exposure for both adult and children. However, other routes of exposure, for instance, dietary intake or dermal absorption via soil may still be prominent in case of Nepal.

1. Introduction

Nitro- and oxy-polycyclic aromatic hydrocarbons (NPAH and OPAHs) are the derivatives of polycyclic aromatic hydrocarbons (PAHs), which contain at least two functional groups such as nitro- and/or carbonyl-functional groups attached with hydrogen on the aromatic ring, respectively (Atkinson and Arey, 1994; IPCS, 2003; Lundstedt et al., 2007). PAH derivatives have been perceived as immediate acting mutagens and cancer-causing agents (Schuetzle, 1983; Lewtas et al., 1990; Durant et al., 1996, 1998; Hannigan et al., 1998; Pedersen et al., 2004, 2005). They have been classified as possible or probable human cancer-causing agents by the International Agency for Research on Cancer (IARC, 1989, 2012). Some PAH-derivatives are more carcinogenic than their parent PAHs (Pitts et al., 1978; Fu et al., 1988; Fu, 1990; Fu and Herrero-saenz, 1999). Hence, an extensive examination/assessment of not only parent PAHs, rather the whole range of their derivative compounds is required to safeguard human and the environment. As of now, majority of the studies reported in literature mainly focused either on parent PAHs, or limited number of nitro-derivative PAHs mostly dealt in air (borne) particulate medium (Albinet et al., 2007; Valle-Hernández et al., 2010; Nassar et al., 2011; Garcia et al., 2014; Liu et al., 2017; Verma et al., 2017; Yang et al., 2017).

In the atmosphere, PAHs can react with pollutants such as ozone, and nitrogen dioxide, yielding diones, and nitro-PAHs, respectively (WHO, 2000). Many of them have been demonstrated to have mutagenic/carcinogenic impact straightforwardly or after biotransformation to hydroxynitro derivative (Neumann et al., 1998; Jinhui and Lee, 2001). A few OPAHs, such as polycyclic aromatic quinones, could create reactive oxygen species that result in oxidative stress leading to allergic disease (Sklorz et al., 2007). Moreover, OPAHs have been subjected to "dead end products" of numerous biological and chemical degradation pathways (Lundstedt et al., 2007), making them more persistent in the environment.

Unlike PAH, which mainly originates from the incomplete combustion of coal, biomass and motor vehicle emissions, OPAHs and NPAHs in the environment can either release together with PAHs or can form through secondary reactions with OH and NO_3 radicals and through homogeneous/heterogeneous reactions with NO_2 (Atkinson et al., 1990; Ringuet et al., 2012; Keyte et al., 2013). Both the NPAHs and OPAHs derivatives are formed primarily as direct or indirect products of incomplete combustion. NPAHs are formed specifically from combustion processes, for example, those in diesel and gasoline engines, as well as indirectly through reactions of PAH with gaseous air pollutants. Likewise, they are valuable tracers for distinguishing the sources of air pollution and/or photochemical pathways (Tang et al., 2005; Alam et al., 2015). Only a few nitro-PAHs are produced industrially, for example, nitronaphthalenes and 5-nitroacenaphthene are commercially produced chemicals.

Most investigation on NPAHs and OPAHs are on air particulate phase (Librando and Fazzino, 1993; Hayakawa et al., 2002; Albinet et al., 2007; de Castro Vasconcellos et al., 2008), little is known about the occurrence, fate, and sources of nitro- and oxy-PAH in house dust. Moreover, the nitro- and oxy-PAHs are significantly more toxic than their parent-PAHs because of their higher molecular weights and considerably different sorption mechanisms (IARC, 1989, 2012). Henceforth, detailed understanding of fate and behavior of NPAHs/OPAH is required. Studies on fate and sources of OPAHs and NPAHs have received worldwide attention in recent years, and field experiments have been led for monitoring OPAHs and NPAHs in different nations. However, the greater part of the research has concentrated on outdoor environments, and little attention has been given to indoor environments which might be especially valuable for revealing the possible health effects. Since individuals invest greater part of their time in indoors (Brauer et al., 2000; Castro et al., 2011; Mentese et al., 2015), indoor air pollution has been perceived as a key public health concern. Indeed, air pollution cannot exclusively be a causative agent for chronic and intense respiratory ailments, yet in addition, it may also affect the medical prognosis of preexisting diseases and conditions (Chen et al., 2004). The main objective of this study is to investigate the concentrations, composition pattern and sources of nitro-, and oxy-PAHs in indoor air and house dust from four major urban areas of Nepal. Additionally, human health risk was estimated to predict the risk of NPAH/OPAH on Nepalese population. To the best of our knowledge, this study is of the first kind to elucidate the fate and sources of NPAHs and OPAHs in indoor air and house dusts of four major Nepalese cities.

2. Materials and methods

2.1. Study area

Four major cities of Nepal (Kathmandu, Pokhara, Birgunj, and Biratnagar) were chosen for gathering the air and dust samples (Fig. 1). Different categories of land use within each urban settlement (such as residential, commercial, public places, office premises, industrial area, high traffic area, occupational area and nearby airport) were focused for collecting the samples. The details about geographical location and sampling sites have been discussed previously (Yadav et al., 2017; Yadav et al., 2018a).

2.2. Passive air sampling

A total of 34 polyurethane foam (PUF) mounted in passive air sampler (PAS) was deployed at preselected sites of four major Nepalese cities (10 in Kathmandu, and 8 each in Pokhara, Birgunj, and Biratnagar, respectively). To expel PAH/NPAH and other organic contaminants already present on PUF resulting from the factory, all the PUF disks were soxhlet extracted with a mixture of acetone and dichloromethane (DCM) (v/v:1/1) at 100 °C and 1500 psi for 15 min to clean and prepare the PUF. After subsequent drying in a vacuum desiccator, the PUF disk was wrapped in aluminum foil, sealed in a zipper bag and transported to the field for deployment. All the PUF-PAS were installed in each city as per standard criteria discussed by Shoeib and Harner (2002) and Jaward et al. (2005). Following an exposure of 60 days, all the PUF disks were retrieved, wrapped and re-sealed in zipper bag before transporting back to the laboratory. In the laboratory, the samples were stored at −20 °C until chemical analysis. Despite the fact that the PUF-PAS sampler may collects some portion of particulate phase of semi-volatile organic compounds (SVOCs), they are generally sampled by active sampler due to high uptake rate. The uptake of SVOCs in the gas phase is governed by diffusion and can be indicated utilizing mass exchange coefficients and rate constants (Bartkow et al., 2005). The uptake of particulate matter is governed by diffusive, gravitational, and inertial process, and the deposition velocity (cm/s) can be anticipated from the particle size distribution (Wagner and Leith, 2001; Nash and Leith, 2010). Since particle phase pollutants are generally connected with the fine and ultrafine particle fractions (Oliveira et al., 2011; Yu and Yu, 2012) and simple PUF-PAS are ideal for collecting SVOCs from the gas phase, and well suited for collecting airborne compounds.