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Nitrated- and oxygenated-polycyclic aromatic hydrocarbon in urban soil from Nepal: Source assessment, air-soil exchange, and soil-air partitioning

Ishwar Chandra Yadav^{a,b,*}, Ningombam Linthoingambi Devi^c^a State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China^b Department of International Environmental and Agricultural Science (IEAS), Tokyo University of Agriculture and Technology (TUAT), 3-5-8, Saiwai-Cho, Fuchu-Shi, Tokyo 1838509, Japan^c Department of Environmental Science, Central University of South Bihar, SH-7 Gaya-Panchanpur Road, Gaya 824236, Bihar, INDIA

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ABSTRACT

In contrast to more frequently investigated priority pollutants, such as polycyclic aromatic hydrocarbons (PAHs), only little is known about the fate and distribution of nitrated- and oxygenated-PAHs (NPAHs and OPAHs) in urban soils, particularly in Indian sub-continent. Moreover, experimental data on air-soil exchange and soil-air partitioning are also lacking, which is critical in assessing the partitioning, fugacity coefficient, and secondary emission of PAH-derivatives. Hence, this article provides an insight into the fate, sources, air-soil exchange, and soil-air partitioning of PAH-derivatives on a molecular basis. Prospective health risk due to their exposure has also been discussed. The result showed that PAH-derivatives had significantly polluted all four Nepalese cities. Σ_{15} NPAHs and Σ_2 OPAHs in soil were 4 and 20 times lower than their parent-PAHs, and ranged 396–2530 ng/g (median 458 ng/g) and 91.9–199 ng/g (median 94.9 ng/g), respectively. Σ_{15} NPAHs was higher than a few global studies, while Σ_2 OPAHs was lower than some of the less urbanized/remote areas worldwide. The 6-Nitrobenzo[*a*]pyrene (6-NBaP) was most abundant in soil, and accounted for 10–12% of Σ_{15} NPAHs, while Benzanthrone (BZONE) exceeded among OPAHs, and represented 71–76% of Σ_2 OPAHs, respectively. Source identification study indicated that direct emissions from domestic/residential cooking and heating and secondary formations are the essential sources of derivative chemicals in soil. Fugacity fraction ratio (f_{ratio}) indicated volatilization from the soil. The soil-air partitioning study showed sorption by soil organic matter/black carbon has little role in soil-air partitioning of PAH-derivatives in Nepal's urban soil. The toxicity equivalency quotients (TEQs) of NPAHs (314 ± 102 ng/g) was estimated slightly higher than their parent-PAHs (294 ± 121 ng/g) suggesting a relatively higher risk of soil toxicity in Nepal.

1. Introduction

Nitrated- and oxygenated-polycyclic aromatic hydrocarbons (NPAHs and OPAHs) are the derivatives of polycyclic aromatic hydrocarbons (PAHs) that contain one or more nitro- or carbonyl functional group (Atkinson and Arey, 1994; Lundstedt et al., 2007). These PAH-derivatives are released into the environment mainly from incomplete combustion of carbonaceous materials such as fossil fuels, biomass, and wastes. The transformations of parent-PAHs through bio-degradation, thermal degradation, and photochemical oxidation reactions may also release PAH-derivative compounds in the environment (Lundstedt et al., 2007; Bandowe and Meusel, 2017; Idowu et al.,

2019). Furthermore, exploration, transportation, and the processing of fossil fuels and petroleum products can release substantial atmospheric PAH-derivatives (Bandowe et al., 2014; Idowu et al., 2019). Reasonably, the PAH-derivatives are more mutagenic than their parent-PAHs (Durant et al., 1996). They are known to cause cancer in humans (IARC, 2012, 2013). Unlike ubiquitous PAHs which are commonly investigated priority pollutants (Devi et al., 2016; Syed et al., 2017; Yadav et al., 2018a, 2018b), only little is known about the fate and environmental effects of PAH-derivatives in urban soil. The soil in urban areas is known to contain a higher concentration of organic pollutants than rural areas due to relatively higher population density, proximity to point source, land use types, and industrial settlements (Wilcke, 2000;

* Corresponding author at: State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China.

E-mail address: icyadav.bhu@gmail.com (I.C. Yadav).

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Bandowe et al., 2010; Bandowe and Wilcke, 2010). Past air monitoring studies have shown an elevated level of PAH-derivatives resulting from anthropogenic activities (Liu et al., 2006; Albinet et al., 2007; Yadav et al., 2018c). Consequently, an elevated level of these derivatives is expected in the soil matrix as it involves movements from and to different compartments (air, soil, and water).

Soil is regarded as the ultimate sinks for many organic pollutants, where they may persist for a longer duration (Wild and Jones, 1995b). Soil pollution in an urban environment mainly results from anthropogenic activities. The atmospheric deposition process can also impact soil pollution (Cousins et al., 1999; Moeckel et al., 2008). The polluted soil can significantly affect human health and the significant ecosystem provided by the earth. These organic pollutants may get transported to surface-water and groundwater through soil, causing drinking water pollution. Soil pollution can reduce food security by reducing crop yield and making crops unsafe for consumption. It can directly harm soil microorganisms and larger soil-dwelling organisms, thereby affecting soil biodiversity. Because of the persistence and semi-volatility behavior of organic pollutants, the previously emitted and deposited compounds can undergo re-emission from the soil until air-soil equilibrium. Studies reported that persistent organic pollutants (POPs) could repeatedly undergo air-surface exchange (Cabrerizo et al., 2011). The air-soil exchange process of organic pollutants in the environment can significantly impacted by various environmental factors such as soil temperature, soil organic matter, the relative humidity of the soil and other meteorological conditions (Cabrerizo et al., 2011; Wang et al., 2011). In contrast to parent-PAHs, studies on the air-soil exchange of derivative compounds are either limited or not available. Also, the sorption characteristic of PAH-derivatives, which is a valuable tool in understanding the fate and transport mechanism, is lacking.

Most studies on PAH-derivatives are about air (gas and particulate phase) (Librando and Fazzino, 1993; Hayakawa et al., 2002; Albinet et al., 2007; de Castro Vasconcellos et al., 2008), dust (Wei et al., 2015a; Yadav et al., 2018c) and aquatic environment (Murahashi et al., 2001; Qiao et al., 2014; Zhang et al., 2014). Only limited studies focused on soil components (Niederer, 1998; Oda et al., 2001; Bandowe et al., 2011, 2018, 2019). The fate and environmental effect of PAH-derivatives in the Indian subcontinent are either not known or very limited. Studies on partitioning and exchange of PAH-derivatives between adjacent ecological compartments, such as air and soil, are also scarce. We hypothesized that the fate and transport of PAH-derivatives in soil could be considerably different from their parent-PAHs because of their relatively higher molecular weights and significantly different sorption mechanisms. Hence, specific knowledge on fate and environmental impact of PAH-derivatives in soil matrix is required. The objective of this study is to investigate the environmental concentration, intercity variation, and sources of selected nitro- and oxy-derivatives of PAHs in soil from four major urban areas of Nepal. Additionally, air-soil exchange, soil-air partitioning, and toxicity potential were discussed.

2. Materials and methods

A detailed description of sampling design and chemical analysis has been discussed in [Supplementary information](#) (S.I.).

2.1. Study city and sampling

A total of 24 top soils (0–10 cm) samples were collected from four major cities (Kathmandu, Pokhara, Birgunj, and Biratnagar) of Nepal, representing the residential, industrial, park and bus station area. Each soil sample was composed of at least three sub-sample collected at a radius of about 5 m in different directions. Detail about sampling cities has been discussed elsewhere (Yadav et al., 2017). After removing the coarse and plant materials, the soil samples were freeze-dried in the laboratory. Later, the soil samples were ground and sieved with a mesh size of 500 μm and stored at $-20\text{ }^\circ\text{C}$ until chemical analysis.

2.2. Extraction and chemical analysis

A total of 26 NPAHs (1-Nitronaphthalene (1-NNAP), 2-Nitronaphthalene (2-NNAP), 1,5-Dinitronaphthalene (1, 5-DNNAP), 1,8-Dinitronaphthalene (1, 8-DNNAP), 1-amino-4-nitronaphthalene (1-ANAP), 5-Nitroacenaphthene (5-NACE), 2-Nitrofluorene (2-NFLU), 2,7-Dinitrofluorene (2,7-DNFLU), 9-Nitrophenanthrene (9-NPHE), 3-Nitrophenanthrene (3-NPHE), 9-Nitroanthracene (9-NANT), 2-Nitroanthracene (2-NANT), 9,10-Dinitroanthracene (9,10-DNANT), 7-Nitrobenzo[a]anthracene (7-NBaA), 2-Nitrofluoranthene (2-NFLUA), 3-Nitrofluoranthene (3-NFLUA), 1-Nitropyrene (1-NPYR), 6-Nitrobenzo[a]pyrene (6-NBaP), 6-Nitrochrysene (6-NCHR), 2-Nitrobiphenyl (2-NBP), 3-Nitrobiphenyl (3-NBP), 4-Nitrobiphenyl (4-NBP), 2,2-Dinitrobiphenyl (2,2-DNBP), 2-Nitrodibenzothiophene (2-NDBT), 3-Nitrodibenzofuran (3-NDBF), and 2,8-Dinitrodibenzothiophene (2, 8-DNDBT)) and 3 OPAHs (i.e. Benzanthrone (BZONE), and Benz [a] anthracene-7,12-dione (BZDIONE)) were selected as target chemicals based on their ubiquitous presence in environment, source indicator, or toxicological importance. Details procedure about extractions, cleaning/purification, and chemical analysis of PAH-derivative chemicals in soil was discussed earlier (Yadav et al., 2018c). Briefly, soil samples were extracted with dichloromethane (DCM) on a soxhlet extraction unit. The extract was then cleaned up and purified into PAH-derivative chemicals by column chromatography. The identification and quantification of NPAHs and OPAHs in the individual extract were made using Gas Chromatography (G.C.) attached with a mass spectrometer (M.S.) operated in selected ion monitoring (SIM) mode. Detail about quality control and quality assurance (QA/QC) is discussed in the S.I. The method detection limits (MDLs) of PAH-derivatives ranged from 22 to 187 pg/g in soil. The average recovery of deuterated- NPAH was 87–101%, 98–111%, 96–112% for 9-NANT-d9, 3-NFLUA-d9, and 6-NCHR-d11, respectively. The average relative standard deviation (RSD) was below 15%. The concentration of PAH-derivatives reported here was blank corrected, but not corrected for recovery. The contamination level of NPAHs/OPAHs was expressed in ng/g on a dry weight basis. Total organic carbon (TOC) and BC were acquired from our previous study (Yadav et al., 2017).

2.3. Fugacity fraction ratio (f_{ratio})

Fugacity fraction ratio (f_{ratio}) is a measure of a chemical's potential to escape from one environmental matrix to another. It is the most commonly used method to indicate the net direction of the exchange of a particular compound between air and surface soil (Cabrerizo et al., 2009; Wang et al., 2015; Yadav et al., 2018d). The fugacity ratio (f_{ratio}) below 0.7 shows deposition in soil, while a greater than 0.7 indicates volatilization out of the soil (Harner et al., 2001). Arithmetically, it is stated as: -

$$f_{\text{ratio}} = f_{\text{S}} / (f_{\text{A}} + f_{\text{S}}) \quad (1)$$

Where, f_{S} and f_{A} refer to soil and air fugacity, respectively. The f_{S} and f_{A} can be further estimated using the following equations (Aliyeva et al., 2012; Degrendele et al., 2016): -

$$f_{\text{S}} = 10^{-9} C_{\text{S}} RT / 0.411 \phi_{\text{OM}} K_{\text{OA}} MW \quad (2)$$

$$f_{\text{A}} = 10^{-9} C_{\text{A}} RT / MW \quad (3)$$

C_{A} and C_{S} are the concentration of individual PAH-derivative in the air (ng/m^3) and soil (ng/g). The fugacity limit of soils is highly dependent on soil organic matter (SOM) (Mackay, 2001), while the fugacity of air is primarily defined as the pollutant concentration in air. In this study, air fugacity was assessed utilizing NPAH and OPAH concentrations reported in our previous study (Yadav et al., 2018c). The soil fugacity was determined using SOM in soil. R denotes universal gas constant ($8.314\text{ Pa m}^3/\text{mol/K}$), T is the average absolute temperature (K) which is the ambient temperature of respective Nepalese cities taken

during soil sampling, ϕ_{OM} refers to the soil organic matter (i.e., 1.5 times of TOC), K_{OA} is the octanol air partition coefficient and was obtained from the literature (Parnis et al., 2015; Bandowe and Meusel, 2017), and 0.411 is the relationship coefficient factor between soil-air partitioning and octanol-air partitioning. The temperature-dependent K_{OA} was obtained from literature was adjusted to ambient temperature in this study.

2.4. Soil-air partitioning

Depending on the chemical properties of compounds and atmospheric conditions, the PAH-derivatives are present in gaseous and particulate phases (Albinet et al., 2008). Soil-air partitioning of organic chemicals is often quantified by their partitioning coefficient (K_{SA}), which is defined as the ratio of mass concentration in soil (ng/g) and the volume concentration in air (pg/m³) (Pankow, 1987). Soil-air partitioning of organic compounds is believed to be controlled by absorption and adsorption, which is related to the particle surface area and TOC/BC content present in soil (Goss and Schwarzenbach, 1998). The soil-air partitioning coefficient K_{SA} (L/kg) can be calculated as (Cabrerizo et al., 2009): -

$$K_{SA} = 1 \times 10^9 C_s / C_A \quad (4)$$

Where, C_s and C_A are the individual concentration of NPAH/OPAH in soil (ng/g) and air (pg/m³), respectively. Moreover, the TOC and BC-based K_{SA} were estimated by the absorption model, which accepts that absorption into the SOM is the essential process responsible for the soil-air partitioning process (Finizio et al., 1997; Ribes et al., 2003).

$$K_{SA} = 1.5(f_{TOC}/\delta_{OCT})K_{OA} \quad (5)$$

Where, f_{TOC} is TOC fraction in soil (g/g dw), δ_{OCT} is the octanol density (0.820 Kg/L at 20 °C), and K_{OA} designates octanol-air partitioning coefficient. To investigate the role of BC in adsorption of PAH-derivatives in soil, the K_{BC-A} model was used (Ribes et al., 2003), and can be expressed as: -

$$K_{SA} = 1.5(f_{TOC}/\delta_{OCT})K_{OA} + f_{BC}K_{BC-A} \quad (6)$$

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

$$\text{Log}K_{BC-A} = -0.85\text{log}P_L + 8.94 - \text{Log}(998/A_{EC}) \quad (7)$$

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

The K_{OA} and K_{BC-A} for PAH-derivatives were obtained from the literature (Parnis et al., 2015; Bandowe and Meusel, 2017) and is given in Table S1, otherwise estimated by EPI-suite (<https://www.epa.gov/ts-ca-screening-tools/epi-suite-estimation-program-interface>; access date: Feb 2020).

2.5. Statistical analysis

The NPAHs /OPAHs concentrations quantified by G.C.-M.S. were processed using MS-excel 2016 and IBM SPSS statistical software (ver 21). The statistical parameters (min, max, mean, and median) and clustered bar graphs were made using MS-excel 2016. Box and whisker plots were created using SPSS. The spatial distribution map was prepared using ESRI's Arc GIS geospatial software (ver 10.3).

2.6. Toxicity equivalency quotient

The toxicity equivalency quotients (TEQs) recommended by the US EPA to assess the toxicity and the carcinogenic risk of the group of chemicals with a similar action mechanism were applied for soil con-

centration data in this study (USEPA, 1993). A toxicity equivalency factor (TEF) is defined as the relative toxicity of a chemical compared to Benzo- α -pyrene (BaP) (USEPA, 1993). BaP is a well-known carcinogen that is used to evaluate the carcinogenic potency of other related chemicals. The TEQs of the NPAHs and OPAHs in ng/g can be estimated by the following equation (8).

$$\text{TEQs} = \sum_{i=1}^n C_i \times \text{TEF}_i \quad (8)$$

Where, C_i is the concentration of individual NPAH/OPAH (ng/g) in dust or soil, and TEF is the toxicity equivalency factor of individual NPAH/OPAH. The TEF was not available for OPAHs, hence only TEQs of NPAHs were estimated in this study. The TEF for individual NPAH was acquired from literature and are presented in Table S1.

3. Results and discussion

3.1. Overall summary

Based on dry weight (dw), only 15 NPAHs (1-ANAP, 5-NACE, 2-NFLU, 2,7-DNFLU, 9-NPHE, 9-NANT, 2-NANT, 9,10-DNANT, 2-NFLUA, 6-NBaP, 6-NCHR, 4-NBP, 2-NDBT, 3-NDBF, and 2, 8-DNDBT and 2 OPAHs (BZONE, and BZDIONE) out of 29 targeted PAH-derivative chemicals (26 NPAHs and 3 OPAHs) were detected in soil (Table S2). Generally, the concentration of Σ_{15} NPAHs in soil was about 4–5 times greater than Σ_2 OPAHs. Σ_{15} NPAHs and Σ_2 OPAHs level in soil in this study ranged from 396 to 2530 ng/g (median 458 ng/g) and 92–199 ng/g (median 94.9 ng/g), respectively (Table S2). The Σ_{15} NPAHs and Σ_2 OPAHs in the soil were about 4 and 20 times lower than their parent-PAHs (median 1810 ng/g), respectively (Yadav et al., 2018b). Studies on the environmental levels of PAH-derivative compounds in urban soil are limited. Even though comparison with previous investigations is mostly affected due to differences in study design, sampling duration, treatment method, and the number of chemicals analyzed, it will give a general view of PAH-derivatives' contamination level across the globe. In this study, Σ_{15} NPAHs and Σ_2 OPAHs in soil were compared with past studies around the world (Table S3 and S4). A significant difference can be seen in these studies. Σ_{15} NPAHs measured in the soil in this study was about 7–11 times greater than those reported in urban soil from Jiaying in China (64 ng/g) (Zhang et al., 2014), and agricultural soil from Eastern China (50 ng/g) (Sun et al., 2017) (Table S3). Furthermore, the Σ_{15} NPAHs in this study were 4–5 orders of magnitude higher than those reported in Gothenburg in Sweden (1.3 ng/g) (Brorström-Lundén et al., 2010) and Basel in Switzerland (0.29 ng/g) (Niederer, 1998) (Table S3). However, the Σ_{15} NPAHs in the soil in this study were consistent that reported in Madrid in Spain (325–378 ng/g) (Priego-Capote et al., 2003). The difference in the contamination level of PAH-derivative in this study with previous studies around the world could be because the semi-volatile organic pollutants (SVOPs) in urban soil can vary from one region to another due to spatial heterogeneity of the soil. Furthermore, the difference in traffic characteristics (density, congestion), fuel formulation and emission control strategy, and meteorological conditions (temperature and relative humidity) can also influence the environmental level of SVOPs.

Oxy-PAHs are other important substituents of parent-PAHs. In this study, Σ_2 OPAHs measured in soil was about 10–14 times greater than previous studies from Manaus in Brazil (7 ng/g) (Bandowe and Wilcke, 2010), Eastern China (9 ng/g) (Sun et al., 2017), but several folds lower than those reported in Kurashiki in Japan, (520–3000 ng/g) (Oda et al., 2001), Angren in Uzbekistan (54–1850 ng/g) (Bandowe et al., 2010), and Bratislava in Slovakia (85–2640 ng/g) (Bandowe et al., 2011) (Table S4). Moreover, the Σ_2 OPAHs in soil (94.9 ng/g) in this study was consistent with those reported in Bangkok in Thailand (98 ng/g) (Bandowe et al., 2014), Xian in China (103 ng/g) (Bandowe et al., 2019), and Basel in Switzerland (120 ng/g) (Niederer, 1998) (Table S4).

3.2. Concentration, profile, and intercity variation of NPAHs

The concentration of individual NPAH chemical measured in the four Nepalese cities has been shown in Fig. 1 and S1. It is evident that the NPAH chemicals are not uniformly distributed in four cities and varied differently. Highest Σ_{15} NPAHs was measured in Birgunj, followed by Kathmandu. Σ_{15} NPAHs in the soil ranged 407–1560 ng/g (median 491 ng/g), 397–1680 ng/g (median 461 ng/g), 408–1490 ng/g (median 561 ng/g), and 408–866 ng/g (median 454 ng/g) in Kathmandu, Pokhara, Birgunj and Biratnagar, respectively. The main reason for intercity variation in the concentration of PAH-derivatives could be due to the different characteristics of the individual city. Birgunj has significant economic importance and is known as the gateway of Nepal, where most trades with India happened through open boarder (CBS/NPCS, 2011). Kathmandu is the capital city with a relatively higher population and urbanization in Nepal. Pokhara is the tourism capital of Nepal, while Biratnagar is the 'industrial capital' of Nepal. Different types of solid fuels, including coal lignite, cow dung flakes and firewood, charcoal, and crop residues, are used in Nepalese houses for domestic cooking/heating and other energy requirements (Pokhrel et al., 2015). Emission from kerosene heater, fuel gas, and liquefied petroleum gas (LPG) used for cooking/heating could be another source of direct emission in Nepal. It is estimated that biomass fuel is one of the most reasonable and economical options for different energy requirements. Roughly, 95% of the total energy necessities in Nepalese houses meet through the burning of biomass fuels (Energypedia, 2016). In 2005, it was estimated that around 17 million tons of wood were used for meeting the various energy demand in Nepal (Surendra et al., 2011; Energypedia, 2016). Likewise, annually about 293,000 tons of coal is used to meet energy requirements in Nepal (Energypedia, 2016). The located graph showing the spatial distribution of NPAHs has been given in Fig. 2 and S2. Individually, the highest concentration of Σ_{15} NPAHs was measured at PKS-3 (1620 ng/g) in Pokhara, KTS-2 (1460 ng/g) in Kathmandu, and BRS-1 (1390 ng/g) in Birgunj. The lowest Σ_{15} NPAHs was detected at PKS-1 (399 ng/g) in Pokhara, BRS-3 (414 ng/g) in Birgunj, and BTS-4 (414 ng/g) in Biratnagar.

The composition profile of NPAHs in the soil in four Nepalese cities is

shown in Fig. 3 and S3. It is evident from Fig. 3 that there was not much difference in the NPAHs composition profile among four cities. Generally, 6-NBaP was the most abundant chemical in soil, followed by 1-ANAP, 3-NDBF, and 5-NACE and accounted for 10–12%, 10–12%, 8–10%, and 6–8% of Σ_{15} NPAHs, respectively (Fig. 3). This finding is in line with a previous study by Bandowe et al. (2019), who also detected an abundance of 1-ANAP and 5-NACE in urban soil from China. The composition profile of NPAHs in soil decreased in the order 6-NBaP > 1-ANAP > 3-NDBF > 5-NACE > 2, 8-DNDBT > 2-NANT > 2, 7-DNFLU > 6-NCHR > 9-NANT > 2-NFLU > 2-NFLUA > 9, 10-DNANT > 9-NPHE > 4-NBP. In Birgunj, the most dominant NPAH was 2-NFLUA, which was slightly different from the rest of the Nepalese cities.

3.3. Concentration, profile, and intercity variation of OPAHs

Box and whiskers plot indicating the contamination level of individual OPAH chemical in the soil in four Nepalese cities has been given in Fig. 1 and S1. Overall, Σ_2 OPAHs in soil ranged from 92.4 to 178 ng/g (median 101 ng/g), 91.9–107 ng/g (median 93.0 ng/g), 92–199 ng/g (median 94.9 ng/g), and 92.2–123 ng/g (median 95.2 ng/g) in Kathmandu, Pokhara, Birgunj, and Biratnagar, respectively. The median concentration of Σ_2 OPAHs in Nepalese cities decreased in the order Kathmandu > Biratnagar > Birgunj > Pokhara. The spatial distribution of Σ_2 OPAHs in the soil in this study has been illustrated in Fig. 2 and S2. Individually, the highest concentration of Σ_2 OPAHs in soil occurred at BRS-1 (199 ng/g) and BRS-6 (128 ng/g) in Birgunj, KTS-2 (178 ng/g) in Kathmandu, and BTS-5 (123 ng/g) in Biratnagar. The lowest level of Σ_2 OPAH was tested at KTS-1 in Kathmandu, PKS-1, and PKS-4 in Pokhara, BRS-3 in Birgunj, and BTS-2 in Biratnagar.

The OPAHs profile in the soil is shown in Fig. 3, and Fig. S3. It is evident from Fig. 3 that the composition of the OPAHs differed slightly from one city to another city. In this study, BZONE was identified as the most abundant OPAH, followed by BZDIONE and accounted for 71–76% and 24–29% of Σ_2 OPAHs, respectively. The 9-FLUONE was measured only in two soil samples from Kathmandu and was dropped from the analysis. This OPAH profile is consistent with the previous studies from

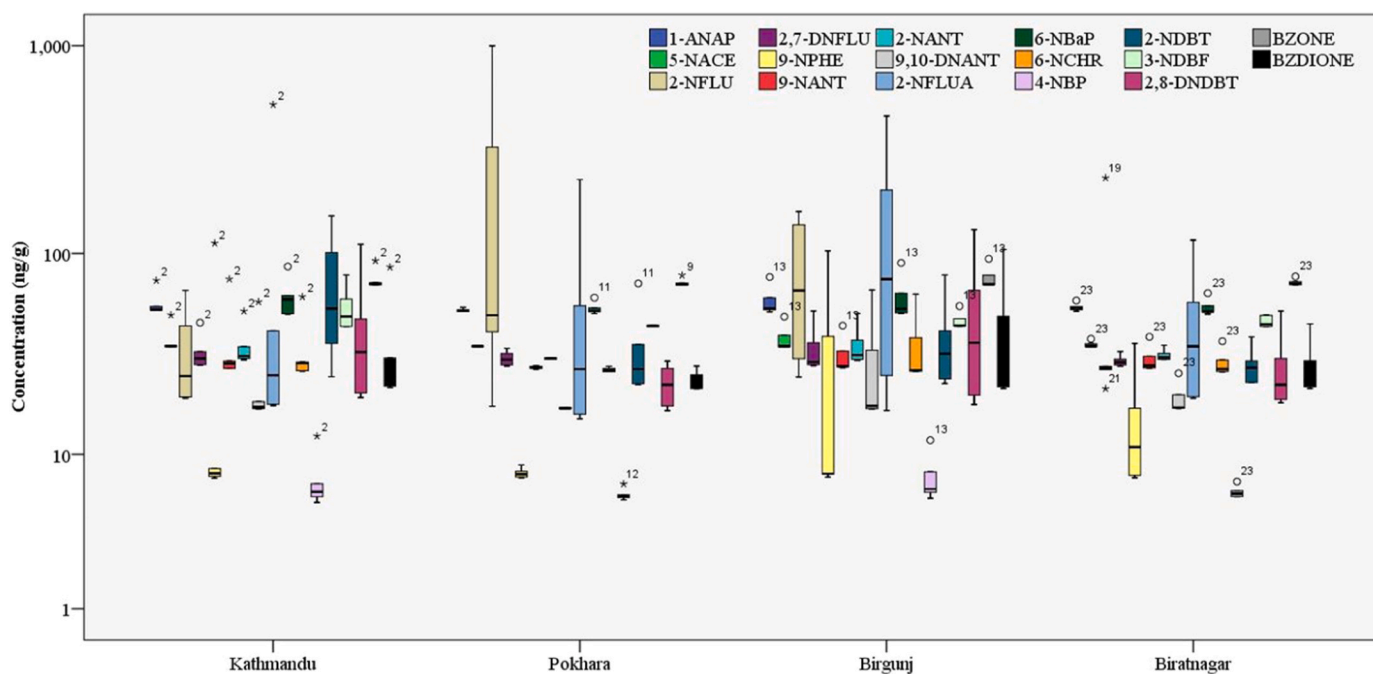


Fig. 1. Box and whisker's plot showing the concentration of NPAH and OPAH in surface soil (ng/g) from Nepal. The central box represents the concentration from 25 to 75 percentile, and the bold middle line represents the median value. The asterisk/stars are extreme outliers that are > 3-times beyond interquartile range. Y-axis is in logarithmic scale.

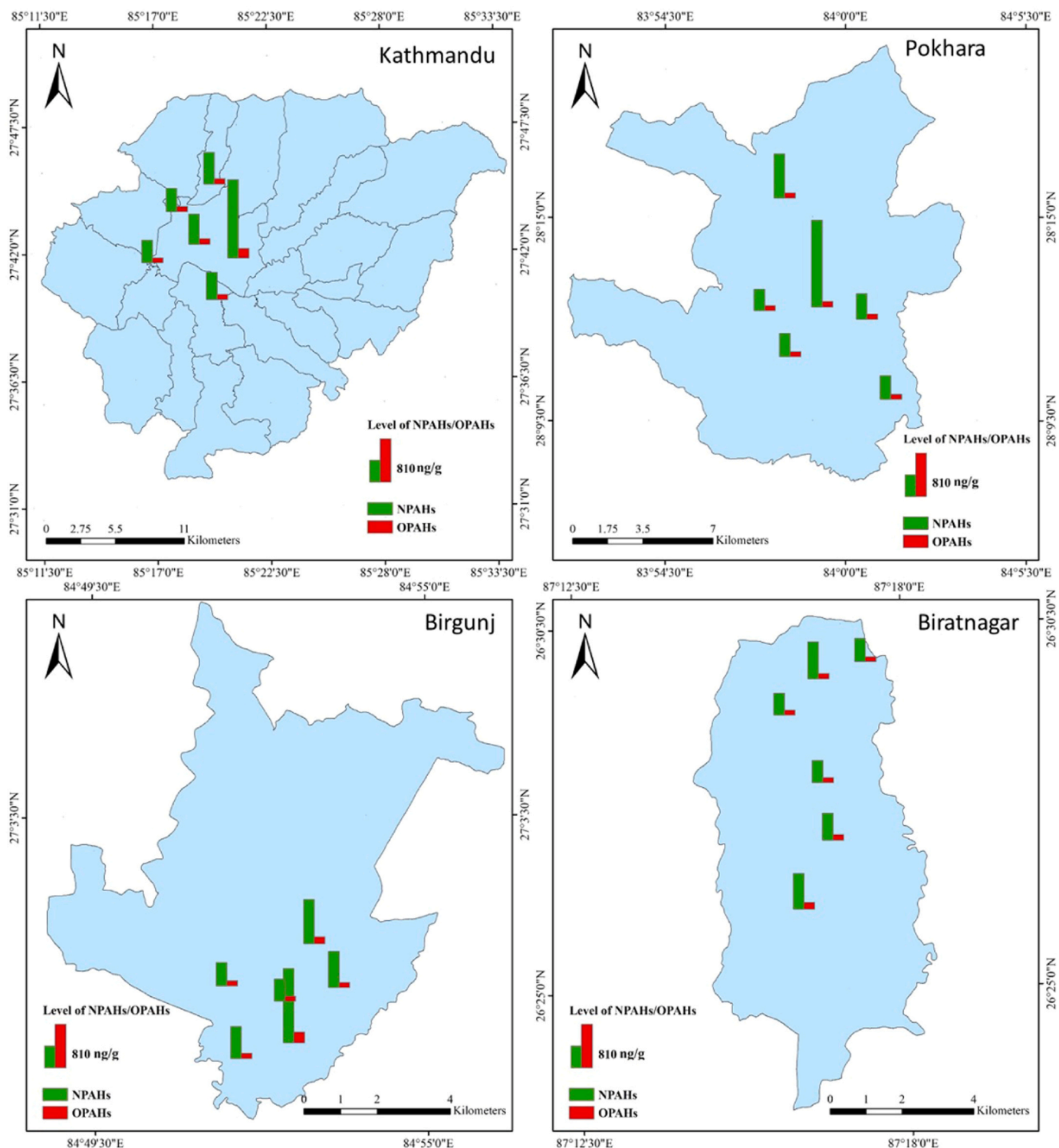


Fig. 2. Spatial distribution of nitrated-PAH and oxygenated-PAH in surface soil (ng/g) from four major cities of Nepal.

Bratislava in Slovakia (Bandowe et al., 2011) and Gothenburg in Sweden (Brorström-Lundén et al., 2010). They also found an abundance of BZDIONE and scant of 9-FLUONE in soil. It is believed that soils affected by combustion-related point sources of pollution will have a higher contribution of high-molecular-weight-OPAH, for instance, BZDIONE. This is because the high-molecular-weight-OPAHs are primarily linked with soil and will settle close to emission sources, while lighter one is subject to long-range atmospheric transport (Albinet et al., 2007, 2008).

3.4. Sources of PAH-derivatives

The source assessment of PAH-derivative chemicals is explicitly limited in the soil matrix (Albinet et al., 2006; Yadav et al., 2018c; Bandowe et al., 2019). The PAH-derivatives in the environment primarily produced as a byproduct of incomplete combustion processes, including biomass burning, domestic/residential heating, street traffic, and industrial process (WHO, 2003a; Shen et al., 2013). In addition to primary combustion sources, the PAH-derivative compounds may also

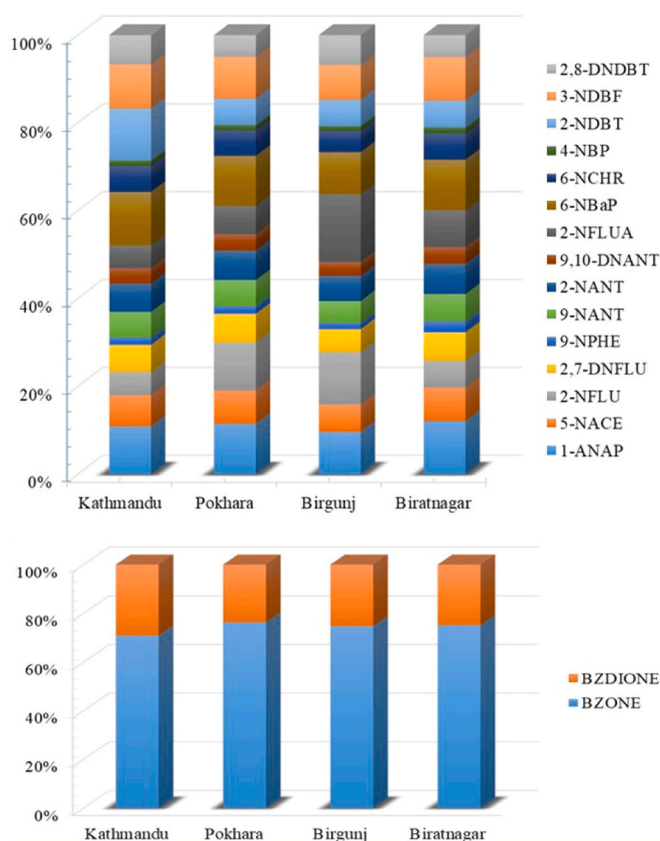


Fig. 3. Compositional profiles of Nitro-PAH and Oxy-PAH in soil from four major cities of Nepal.

release from secondary formation processes (Atkinson et al., 1990; Fan et al., 1995). Although the complete and accurate source identification of PAH-derivatives is a difficult task, the molecular diagnostic ratio of individual PAH-derivatives to their corresponding parent-PAHs provides some perspective toward source assessment. This concentration ratio is considered one of the widely accepted approaches to studying the sources mechanism (Albinet et al., 2008; Kim et al., 2012; Wei et al., 2015a). In this study, the concentration ratios of $\Sigma_{15}\text{NPAHs} / \Sigma_{16}\text{PAHs}$, $\Sigma_2\text{OPAHs} / \Sigma_{16}\text{PAHs}$ and individual NPAH and/or OPAH to their parent-PAH were estimated to track the potential formation of the PAH-derivatives from their parent compounds (Table S5). The concentrations ratios of $\Sigma_{15}\text{NPAHs} / \Sigma_{16}\text{PAHs}$ and $\Sigma_2\text{OPAHs} / \Sigma_{16}\text{PAHs}$ were significantly lower than 1 in soil. This indicates a substantial contribution of NPAHs and OPAHs from parent-PAHs via degradation processes (Glaser et al., 2005). This is true in the case of a tropical country like Nepal, where the ambient temperature is relatively higher than in other regions. This finding is in line with the previous study by Wei et al. (2015a), who also suggested a significant contribution from the secondary formation. A similar concentration ratio was observed for individual NAPH and OPAH, except 5-NACE and 2-NFLU (Table S5). The concentration ratio of 5-NACE/ Acenaphthalene and 2-NFLU/ Fluorene was > 1 , illustrating the abundance of NPAHs/OPAHs relative to their parent-PAHs. The individual NPAH or OPAH/parent-PAH concentration was not the same across all cities, suggesting multiple sources (primary and/or secondary) in soil.

The concentration ratio of 2-NFLUA to 1-NPYR is another essential approach widely used for evaluating the relative contribution of direct emission versus secondary formation (Zielinska et al., 1989; Bamford and Baker, 2003). 2-NFLUA is produced only from the gas-phase reaction between fluoranthene and NO_2 initiated by O.H. during the day and started by NO_3 during the night. 1-NPYR only originates from any known gas-phase reaction. The 2-NFLUA/1-NPYR ratio greater than 5

shows the contribution from secondary formations, while a 2-NFLUA/1-NPYR ratio below 5 indicates the direct emission (Bamford and Baker, 2003). In this study, 1-NPYR was below MDL in the soil bringing about a high estimation of 2-NFLUA. This suggests the dominance of secondary formation (Fig. 4). This is further backed by the fact that parent-PAHs (median 1810 ng/g) in soil (Yadav et al., 2018b) were significantly higher than their nitro-derivative (median 458 ng/g) and oxy-derivative compounds (median 94.9 ng/g). A high concentration of parent-PAHs is likely to yield PAH-derivatives on degradation (Li et al., 2014).

In summary, we conclude that direct emissions from domestic/residential cooking and heating together with the secondary formation of parent-PAHs are the essential sources of elevated level of PAH-derivatives in the soil of Nepal.

3.5. Air-soil exchange of NPAH/OPAH

The comparison of air and soil fugacity infers the direction of air-soil exchange. When fugacity in soil is greater than air, there is net volatilization of organic pollutants, while higher air fugacity than soil fugacity is indication of net deposition. In this study, the result of the air-soil exchange based on the fugacity fraction ratio of NPAH and OPAH compounds has been indicated in Fig. 5. Fig. 5 shows large variation soil fugacity for high molecular weight (HMW) chemicals with 3-NDBF, 4-NBP especially at Pokhara and Birgunj. It is evident from Fig. 5 that the soil to air fugacity (f_{ratio}) estimated for PAH-derivatives were well above 0.7, unequivocally showing the net volatilization of derivative-PAHs from soil. Studies on the air-soil exchange of PAH-derivative compounds are limited. This outcome is in line with the air-soil exchange of halogenated flame retardants compounds in the same study area (Yadav et al., 2018d).

3.6. Soil-air partitioning of NPAH/OPAH

The transport and fate of derivative-PAHs in soil is highly dependent on their sorption mechanism to soil amorphous organic matter and black carbon by nonspecific hydrophobic interactions (Murakami et al., 2008; Tomaz et al., 2017). In soil, TOC and BC are the two critical factors governing the adsorption (or absorption) kinetics of organic compounds, including PAH-derivatives (Goss and Schwarzenbach, 1998). In this study, the temperature-dependent octanol-air partitioning and black carbon-air partitioning was estimated using Eqs. (5) and (6). The temperature-dependent $\text{Log } K_{\text{OA}}$ and $\text{Log } K_{\text{BC-A}}$ were studied as the predictor of the measured $\text{Log } K_{\text{SA}}$ (Fig. 6). Absorption into the organic

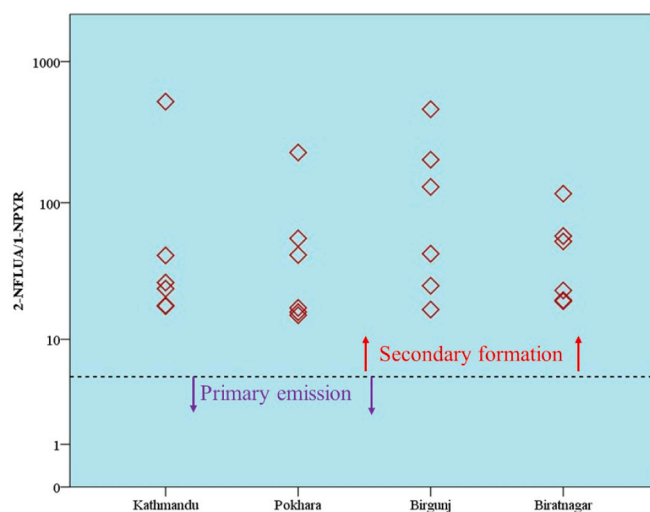


Fig. 4. Cross plots of the isomeric ratio of 2-NFLUA/1-NPYR used for source identification of NPAH in surface soil.

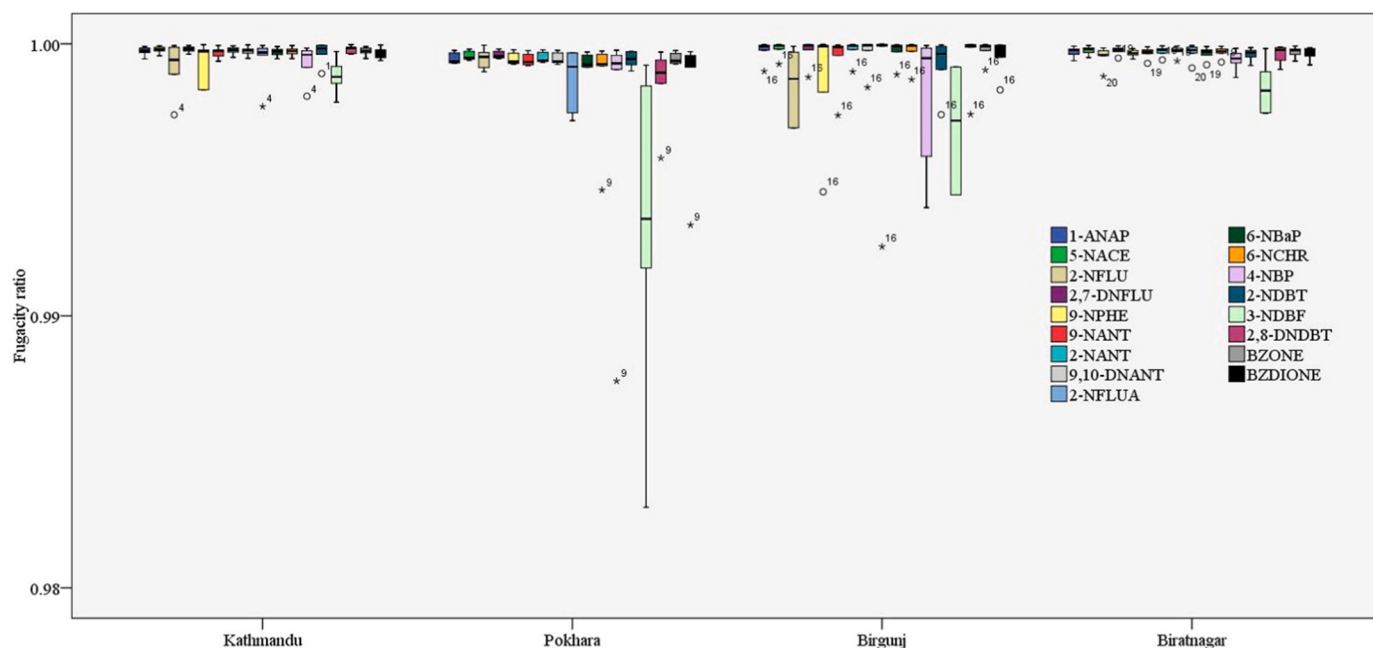


Fig. 5. Box and whisker plot show a fugacity fraction of PAH-derivative compounds in Kathmandu, Pokhara, Birgunj, and Biratnagar. The central box represents the concentration from 25 to 75 percentile, and the bold middle line represents the median value. The asterisk/stars are extreme outliers that are > 3-times beyond interquartile range.

matter in soil and adsorption onto the surface of the soil seems weak as indicated by the slope value (Fig. 6). The measured $\log K_{SA}$ was weakly related to $\log K_{OA}$ ($R^2 = 0.185$) and $\log K_{BC-A}$ ($R^2 = 0.244$), implying that soil-air partitioning is little governed by absorption/adsorption on SOM. The relationship between PAH-derivatives and TOC/BC can be attributed to co-emission, co sorption, co-deposition and similar post-emission transport and fate (Han et al., 2015; Wei et al., 2015a). This is because the LMW compounds are generally more dominant in gaseous phase and are likely to undergo equilibrium between air and SOM. Also, BC has higher surface area and strong affinity to non-polar compounds like derivative-PAHs. The HMW derivatives are precursor of combustion process and can be co-emitted with BC into the atmosphere (Wei et al., 2015a). This suggests neither octanol-air partitioning nor black carbon- partitioning is a suitable surrogate for SOM. Hence, there is little risk that derivative-PAHs can reach groundwater. Additionally, to model the fate of PAH-derivatives as a function of absorption by SOM, the measured K_{SA} in this study was plotted against predicted K_{SA} from K_{OA} and K_{BC-A} (Fig. 6). The predicted result were found generally underestimated for derivative-PAH compounds. The discrepancies between measured and predicted result could be due to non-equilibrium gas/particle partitioning. The measured K_{SA} was ineffectively connected with predicted K_{SA} from K_{OA} and K_{BC-A} , suggesting that SOM retention has little/no role in the soil-air partitioning of PAH-derivatives in the soil of Nepal. This finding is in line with gas/particle partitioning study from northern China (Li et al., 2016). It is opined that partitioning model generally underestimate the K_{SA} , hence the results are not strongly supporting the mechanism of air-soil partitioning.

3.7. Toxicological impact of PAH-derivatives

In this study, the TEQ was estimated for five NPAH compounds only. The rest compounds were not assessed for their risk because of the unavailability of TEF values. The average TEQ for NPAHs in soil was estimated as 314 ± 102 ng/g, which is slightly higher than TEQ of parent-PAHs (294 ± 121 ng/g) (Yadav et al., 2018b), indicating relatively greater risk. The individual TEQ for five different NPAHs were: 5-NACE (1.11 ± 0.12 ng/g), 2-NFLU (1.05 ± 2.04 ng/g), 9-NANT

(0.10 ± 0.03 ng/g), 2-NFLUA (0.23 ± 0.35 ng/g), and 6-NCHR (312 ± 102 ng/g). The TEQs of 5-NACE, 2-NFLU and 6-NCHR were higher than the WHO standard limit (1 ng/g). Highest TEQ was estimated for Birgunj (average 351 ± 149 ng/g), followed by Kathmandu (339 ± 138 ng/g), Biratnagar (293 ± 43 ng/g), and Pokhara (273 ± 8.6 ng/g), respectively.

4. Conclusions

In this study, the contamination level, distribution pattern, and sources of nitrate-PAH and oxy-PAH were investigated in surface soil from four major urban areas of Nepal. Σ NPAH and Σ OPAH levels in soil were about 4 and 20 times lower than their parent-PAHs, respectively. Σ NPAH in the soil in this study was higher than a few studies but consistent with some of the contaminated soil. Source assessment study suggested an elevated level of PAH-derivatives in soil could result from combined sources i.e., direct emission (from domestic/residential cooking and heating) and the secondary formation of parent-PAHs. The fugacity fraction ratio indicated the volatilization of PAH-derivatives from the soil. The soil-air partitioning study suggested that the absorption/adsorption of soil organic matter either didn't affect or poorly affected the soil-air partitioning of PAH-derivatives in Nepal's soil. The estimated TEQ for NPAH was slightly higher than TEQ of parent-PAH, suggesting a relatively more significant risk. Since this study estimated risk for only five NPAH because of the absence of TEF values for other abundant NPAHs (such as 9-NPHE), the TEQ result underestimated the risk. Hence, more toxicological studies on PAH-derivatives are required for accurate risk assessment.

CRedit authorship contribution statement

Ishwar Chandra Yadav: Design, methodology, original draft preparation, writing- reviewing and editing. **N.L. Devi:** Conceptualization, Data curation, investigation, reviewing and editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial

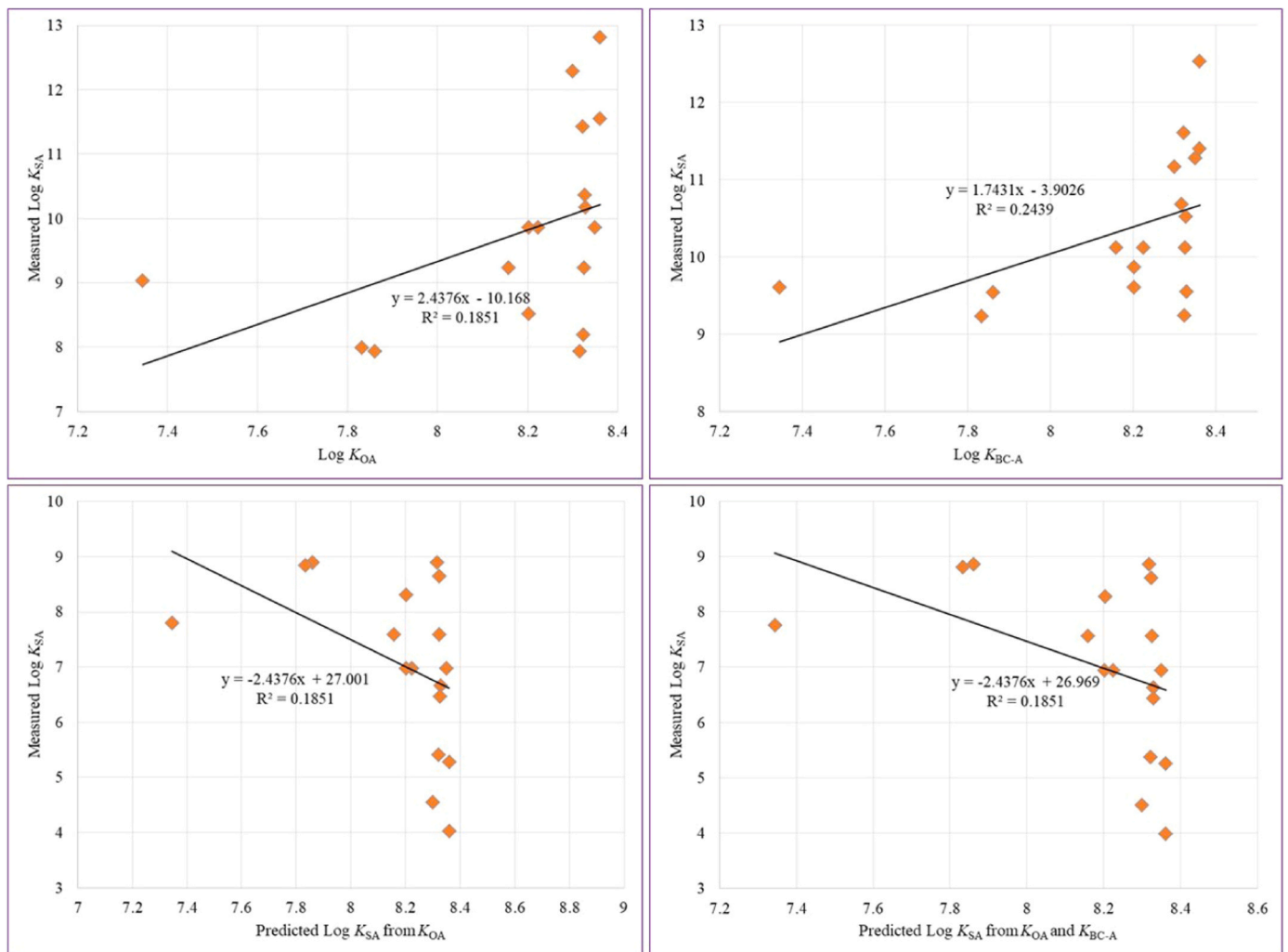


Fig. 6. Influence of Log K_{OA} and Log K_{BC-A} on measured Log K_{SA} (top), and comparison of measured and predicted K_{SA} (bottom).

interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.ecoenv.2021.111951](https://doi.org/10.1016/j.ecoenv.2021.111951).

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