AJAE

Open Access

Vol. 15, No. 4, 2021101, December 2021
doi: https://doi.org/10.5572/ajae.2021.101
ISSN (Online) 2287-1160, ISSN (Print) 1976-6912

Research Article

Characteristics of Atmospheric Particle-bound Polycyclic Aromatic Compounds over the Himalayan Middle Hills: Implications for Sources and Health Risk Assessment

Linda Maharjan[1),2)], Lekhendra Tripathee[1),3),*], Shichang Kang[1),2),4)], Balram Ambade[5)], Pengfei Chen[1)], Huijun Zheng[1),2)], Quanlian Li[1)], Kundan Lal Shrestha[6)], Chhatra Mani Sharma[7)]

[1)]State Key Laboratory of Cryospheric Science, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, Lanzhou, China
[2)]University of Chinese Academy of Sciences, Beijing, China
[3)]Himalayan Environment Research Institute (HERI), Kathmandu, Nepal
[4)]Center for Excellence in Tibetan Plateau Earth Sciences, CAS, Beijing, China
[5)]Department of Chemistry, National Institute of Technology Jamshedpur-831014, India
[6)]Department of Environmental Science and Engineering, Kathmandu University, Dhulikhel, Nepal
[7)]Central Department of Environmental Science, Tribhuvan University, Kathmandu, Nepal

***Corresponding author.**
Tel: +86-13522729428
E-mail: lekhendra.t@gmail.com

Received: 23 August 2021
Revised: 23 September 2021
Accepted: 24 September 2021

ABSTRACT This study was conducted in the Central Himalayan middle hills to understand the nature of polycyclic aromatic hydrocarbons (PAHs) embedded in aerosol particles, their sources and human health risk assessments. The level of sum of 15 particle-phase PAHs was between 9 and 335 ng/m^3, with an average concentration of 73±66 ng/m^3. There were strong seasonal differences in total suspended particles (TSP) and particle-bound PAH concentrations with higher concentrations in winter, followed by pre-monsoon and lowest in monsoon. The main contributor to the suspended particles was 5-ring PAHs (32%), followed by 4-ring (29%), 6-ring (28%), and 3-ring PAHs (11%). Conversely, the gas-phase PAHs showed that 3-ring PAHs contributed utmost to the total particles. The molecular ratios and principal component analysis indicated that both petrogenic and pyrogenic sources, particularly fossil fuel combustion, biomass combustion, and car exhausts, were the major sources of PAHs. The overall average Benzo (a)pyrene equivalent concentration of particulate PAHs was 11.71 ng/m^3, which substantially exceeded the WHO guideline (1 ng/m^3), and indicated the potential health risks for local residents. The average lifetime inhalation cancer risk (ILCR) estimates associated with carcinogenic PAHs was 8.78×10^{-6} for adults, suggesting the possible cancer risk and 2.47×10^{-5} for children, signifying extreme carcinogenic effects of PAHs on children's health. Therefore, strict measures should be taken to reduce PAHs emissions in the region.

KEY WORDS Aerosol, Polycyclic aromatic hydrocarbons, Long-range transport, Himalayas, Nepal

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic contaminants with two or more fused aromatic rings that originate from incomplete burning of organic matter (Rajput *et al.*, 2014; Singh *et al.*, 2013; Zhang and Tao, 2009). They are considered to have remarkable mutagenic, carcinogenic, and teratogenic properties due to the presence of aromatic rings (Suvarapu *et al.*, 2012; IARC, 2010). Moreover, PAHs are unaffected by biodegradation, and due to their hydrophobic

characteristics and low solubility, they can bio-accumulate in the ecosystems (Zhu *et al.*, 2008; Conde *et al.*, 2005). The origins of PAHs in the environment include anthropogenic and natural sources. Volcanoes, forest fires, earth's thermal and geologic permutations include natural sources (Juhasz and Naidu, 2000), while human activities include the incomplete combustion of fossil fuels (petroleum, oil, coal, gas), domestic and commercial heating with biomass (wood and others), industrial exhausts, vehicular traffic emissions (motor vehicles exhaust), waste incineration, and tobacco smoke (Maharjan *et al.*, 2022; Kamal *et al.*, 2015; Chang *et al.*, 2006). PAHs and their metabolites are of great concern because of their presence by widespread sources and persistence in air, water, and soil and, importantly, their toxicity and harm to human, animal, and plant health (Kim *et al.*, 2013; Ravindra *et al.*, 2008). On the basis of their carcinogenic potency, the United States Environmental Protection Agency (USEPA) has identified 16 priority PAHs: including Naphthalene (NaP), Acenaphthylene (AcPy), Acenaphthene (AcP), Fluorene (Flu), Phenanthrene (Phe), Anthracene (AnT), Fluoranthene (FluA), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chr), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno(1,2,3-cd) pyrene (IndP), Dibenzo(a,h)anthracene (DbA), and Benzo(g,h,i)perylene (BghiP).

Several studies have been conducted on aerosol chemical characteristics (e.g., soluble ions, carbonaceous species, and particulate mercury) over the Indo-Gangetic Plains (IGP) and Himalayan areas (Guo *et al.*, 2022, 2020, 2017; Tripathee *et al.*, 2021, 2017, 2016; Chen *et al.*, 2020, 2019). However, limited studies exist on the chemical composition of aerosol particles over the middle hills of the Himalayas, where there are regional and local impacts on aerosol chemistry. Besides, there have been sparse studies reported on the concentrations, deleterious nature of airborne PAHs and their adverse impacts on human health in the middle hills of the Central Himalayas, though much research has pointed out that the urban aerosols from polluted surrounding areas have posed a potential threat to lives and ecosystems (Chen *et al.*, 2017, 2015). Meanwhile, PAH concentrations in soils were presented in a central Himalayan region (Bi *et al.*, 2016), which suggested that the big cities had the highest PAH levels, while the high Himalayas had the lowest (Bi *et al.*, 2016). The PAHs of lower molecular weight are volatile and found chiefly in the gas phase, while the higher molecular weight PAHs are usually found to be attached to particulate matter (Yang *et al.*, 2018; Lee *et al.*, 2001). These compounds exhibit a wide range of gas-particle partitioning characteristics in the air, which plays a fundamental role in controlling their fate, transport, variation, and removal mechanisms through dry and wet deposition courses (Esen *et al.*, 2019; Harner and Bidleman, 1998). Various factors, such as ambient temperature, relative humidity, liquid vapor pressure, the composition of chemicals, and the nature of the particles affect the partitioning behavior of PAHs (Gaga *et al.*, 2012). Understanding the gas/particle-phase distribution of PAHs in the atmosphere is important for environmental as well as health risk evaluation, as some of the species are considered to be carcinogenic even at lower concentrations. Nevertheless, we are still unaware of this partitioning distribution of PAHs over the study region. Therefore, it is important to well understand the composition, characteristics, origins, and transport of atmospheric contaminants (e.g., PAHs) and their impacts on human health and the ecosystems in this region. Moreover, this study is also important as the contaminants (e.g., PAHs, mercury, black carbon etc.) could be easily transported to the glaciers and pristine ecosystems of the Himalayan Tibetan Plateau (HTP) as evidenced from prior studies (Chen *et al.*, 2019; Kang *et al.*, 2019; Tripathee *et al.*, 2019). The HTP glaciers act as the archive of contaminants deposited through wet and dry deposition from the heavily polluted South Asian regions. The glacier melting from the HTP releases such deposited pollutants to glacier rivers on which a large population downstream relies for fresh water, thereafter impacting the health of the residents and the whole ecosystems (Zhang *et al.*, 2017). Therefore, understanding is important of the fate and characteristics of atmospheric contaminants like PAHs over the South Asian regions, especially in the mid-hills of the Himalayas with limited local sources.

Under the Atmospheric Pollution and Cryospheric Changes (APCC) network (Kang *et al.*, 2019), this research presents the results of 15 priority PAHs in the particulate phase from TSP samples in Dhulikhel, Nepal, collected from the period of January to July 2018. This study is intended to determine the concentrations, seasonality and to recognize the possible sources of PAHs in atmospheric particulate samples from characteristic molecular ratios and principal component analysis (PCA). Furthermore, the study aimed to evaluate the carcinogenic health risks from the atmospheric PAHs by inhalation in the study site. The results of this study are useful for the con-

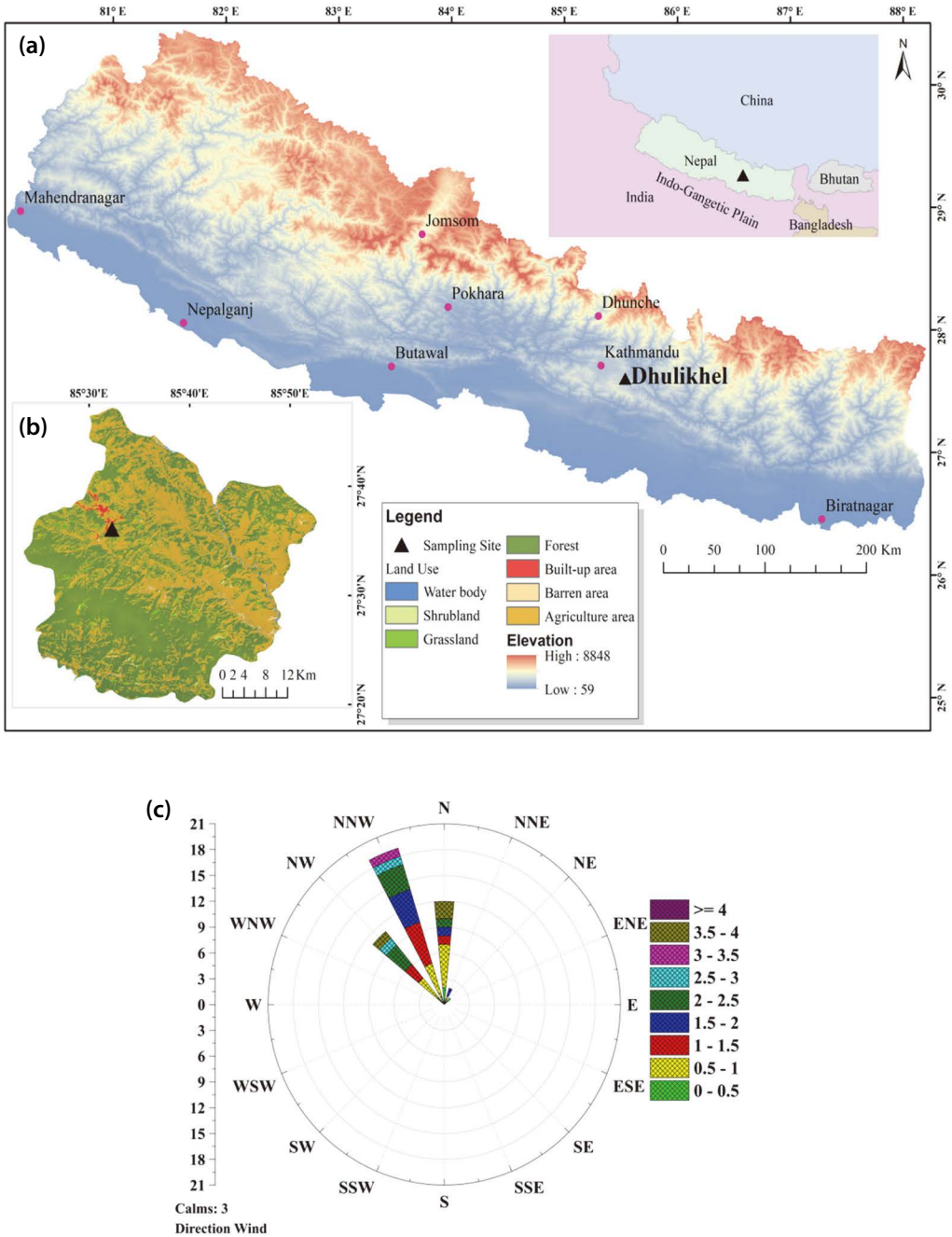

Fig. 1. Location of the sampling site (Dhulikhel) in Nepal. (a) Sampling site, (b) Land use map showing the sampling location with black triangle, (c) Wind rose diagram during the sampling period.

trol and management of atmospheric PAHs in the region.

2. MATERIALS AND METHODS

2. 1 Study Area and Collection of Samples

The sampling was performed within the premises of Kathmandu University, located near Dhulikhel, a town in the central Himalayan middle hills, Nepal (Fig. 1). The sampling location (27.601°N, 85.538°E, 1,510 m) lies about 25 km southeast which is upwind of the major leading city of Kathmandu Valley, Nepal. The capital city, Kathmandu, is a heavily polluted urban location, with

nearly more than 2 million inhabitants. Banepa is another major town, which is located about 2.5 km northwest of the study area. Previous studies have ascribed that Dhulikhel is impacted by the extensive pollutant transport from the highly polluted IGP region as well as local sources from nearby urban cities (Tripathee *et al.*, 2021; Shrestha *et al.*, 2010). Temperature and relative humidity at the study location during the study phase is displayed in Fig. S1. The temperature was noted to be warm and humid during summer and cold and dry during the winter.

Aerosol sampling was carried out from January to July 2018. The total suspended particulate (TSP) sampler was established on the rooftop of the building (15 m above ground) of Kathmandu University bounded by agricultural fields, residential housing, and forests with limited local emissions. Overall, 48 TSP samples were collected with the Qingdao Laoying TSP Cyclone (T2034) at 100 L/min of flow rate for 24 hours (Tripathee *et al.*, 2021; Chen *et al.*, 2019). Briefly, the sample collection was done on pre-combusted quartz fiber filters (diameter 90 mm, Whatman, Maidstone, UK). The quartz fiber filters were pre-combusted (550°C, 6 h) to lessen any residual organic matter. During the pre-monsoon season, 2 to 3 samples were taken each week to capture the heavy pollution loadings during dry periods, and during other periods, one sample per week was taken. The collected samples were relocated to a clean disc and kept in a freezer prior to the laboratory analysis. The weight of all quartz filters was evaluated gravimetrically before and after the sampling to obtain the aerosol mass concentrations.

2.2 PAHs Extraction and Analysis

This study followed the procedure for extracting and analyzing PAHs according to the prior research (Maharjan *et al.*, 2022; Chen *et al.*, 2015). For the pre-treatment of PAHs, 5.08 cm^2 of each filter was cut and sited in a sample bottle and was submerged in a mixed solution (20 mL) of dichloromethane (DCM) and n-hexane (1 : 1). Sonicating the mixtures ultrasonically thrice each for 30 minutes was done. Spiking of each sample was done with deuterated PAH, Chrysene-d12 as recovery surrogates, and was left for about 30 minutes. With a rotary evaporator, the mixtures obtained were then concentrated to about 0.5 mL and were moved into a multi-layered column containing active silica gel, neutral alumina, and Na_2SO_4 (anhydrous). Then, n-hexane (10 mL) and mixed solution (1 : 1) of DCM/n-hexane (20 mL) was poured to elute the column. After that, the solvent was blown underneath the nitrogen gas stream to get 1 mL ultimate volume. The final solution was then moved to a sample vial to be measured. Samples were examined for the 15 priority PAHs (USEPA classified) by using Gas chromatography-mass spectrometry (GC-MS). Further details on full methods and quality control and assurance have been presented in the Supplementary text (Text S1).

2.3 Estimation of PAHs Gas/Particle Partitioning

The PAHs partitioning among the gas and the particle phase can be approximated from its octanol-air partition coefficient (K_{OA}). The K_{OA} values for PAHs can be determined from the method of gas chromatographic retention time as given in equation 1 (Harner and Bidleman, 1996):

$$\log K_{OA} = A + (B/T) \quad (1)$$

where the parameters of regression, dependent on temperature, are given as A and B (Odabasi *et al.*, 2006; Harner and Bidleman, 1998). Table S1 lists different K_{OA} of PAHs in the sampled periods as estimated by modifying the equation to the ambient temperature (average) in the study site (winter: 10°C, pre-monsoon: 18°C, and monsoon: 23°C).

K_P, the gas-particle partition coefficient is expected using K_{OA} in equation 2, assuming that the principal distribution course is absorption (Ayyildiz and Esen, 2020; Wang *et al.*, 2013; Harner and Bidleman, 1998):

$$\log K_P = \log K_{OA} + \log f_{OM} - 11.91 \quad (2)$$

where the fraction of organic matter on TSP is given by f_{OM}. The average organic carbon (OC) concentrations in aerosols in this study were 25.92, 21.62, and 7.65 $\mu g/m^3$ for winter, pre-monsoon, and monsoon seasons, respectively. OM was calculated based on OC values using the equations in the previous study in Himalayas and Tibetan Plateau (Chen *et al.*, 2018, 2015):

$$OM = OC \times 1.6$$

$$f_{OM} = OM/\ TSP$$

$$f_{OM} = (OC \times 1.6)/TSP$$

The transformation of OC values to organic matter (OM) contributed about 12.42%, 12.41%, and 8.54% to the total suspended particles in the respective sampled seasons. Using the K_P value ($m^3\ \mu g^{-1}$), atmospheric PAHs distribution between the particle and gas phases is

given as follows:

$$K_p = (C_p / C_{TSP})/C_g \quad (3)$$

where and C_g and C_p (ng/m^3) are the concentration of PAHs in the gaseous and particle phases, respectively, and C_{TSP} (μg/m^3) is the total aerosol particles concentration in air (Verma *et al.*, 2017; Harner and Bidleman, 1998).

2.4 Assessment of Health Risk

Human health risk/threat assessment can be done using human exposure to PAHs occurring through the routes of inhalation, ingestion, or dermal contact (USEPA, 1989). The inhalation of particulate PAHs in the air was taken into account for the carcinogenic risk assessment in this study. For estimating the health risks related to exposure of PAHs, the Benzo(a)pyrene equivalent concentration (BaP_{eq}) is used and it is based on carcinogenic potencies of individual PAHs relative to BaP (Chen *et al.*, 2016; Nisbet and Lagoy, 1992). The toxicity equivalency factor (TEF) of each PAH relative to BaP carcinogenic strength multiplied by its corresponding concentration determines the BaP_{eq} of each PAH (ng m^{-3}) as given by the equation below:

$$\text{Total } BaP_{eq} = \Sigma_i (C_i \times TEF_i) \quad (4)$$

The lifetime average daily dose (LADD) of PAHs is the intake quantity per kilogram of body weight per day of a pollutant which has the potential of causing adverse health impacts once the body absorbs it over a long time span (mg/kg/day). The incremental lifetime cancer risk (ILCR) is determined using the LADD of PAHs. The details on the estimation of LADD are given in the Supplementary text (Text S2). The equation for estimating ILCR (Bortey-Sam *et al.*, 2015; Jamhari *et al.*, 2014) is shown as follows:

$$ILCR = LADD \times CSF \quad (5)$$

where CSF denotes the cancer slope factor and its value of 3.14 (mg^{-1} kg day) is taken in this study (Chen and Liao, 2006). The standard values were acquired from USEPA (2011).

Also, the Lifetime Lung Cancer Risk (LLCR) through inhalation exposure to PAHs is estimated by the equation given below as used by Chen *et al.* (2017):

$$LLCR = \Sigma BaP_{eq} \times UR_{BaP} \quad (6)$$

where UR_{BaP} denotes the cancer unit risk by BaP inhalation and the value is 8.7×10^{-5} as specified by the World Health Organization (WHO).

3. RESULTS AND DISCUSSION

3.1 Overview and Seasonal Characteristics of TSP and PAHs

The overview of the mean ΣPAHs concentrations and ambient TSP in the study area, Dhulikhel, is presented in Table 1. The comparison of average concentrations of PAHs at Dhulikhel with other regions worldwide is shown in Fig. 2. The sum of PAHs and aerosol mass concentrations during the study period ranged from 9 to 335 ng/m^3 and 62 to 442 μg/m^3, respectively. The average concentration of total PAHs obtained in Dhulikhel (73 ± 66 ng/m^3) was similar to those reported in other places of Asia, such as Eerduosi, China (Wu *et al.*, 2014), Nanjing, China (Wang *et al.*, 2006), rural Jamshedpur, India (Kumar *et al.*, 2020), and Kolkata, India (Ray *et al.*, 2017) but lower than the ones reported in Kathmandu, Nepal, a heavily polluted urban city (Chen *et al.*, 2015), and a typical rural site in Nepal, Lumbini (Chen *et al.*, 2016). The values were also lower than the reported levels in other cities of India such as Delhi, (Sarkar and Khillare, 2012), Amritsar, (Kaur *et al.*, 2013), Agra (Rajput and Lakhani, 2012), and in China, Beijing, (Wang *et al.*, 2008). The

Table 1. Summary of total concentration of particle-bound PAHs (ng/m^3) and TSP (μg/m^3) in the study site.

S.N	PAHs	Ring	Mean	SD	Minimum	Maximum
1	AcPy	3	0.38	0.33	0.00	0.92
2	AcP	3	0.81	0.44	0.19	1.52
3	Flu	3	2.29	0.56	1.24	4.04
4	Phe	3	3.67	0.83	2.25	6.21
5	AnT	3	0.57	0.34	0.18	1.14
6	FluA	4	5.30	4.35	1.08	17.93
7	Pyr	4	5.91	5.59	0.77	24.10
8	BaA	4	4.30	3.93	0.03	14.85
9	Chr	4	5.96	5.68	0.61	23.83
10	BbF	5	9.27	7.49	0.18	34.87
11	BkF	5	5.76	5.14	0.02	27.07
12	BaP	5	7.82	7.83	0.59	37.14
13	IndP	6	9.49	10.15	0.88	56.19
14	DbA	5	0.82	0.49	0.29	2.47
15	BghiP	6	10.84	13.30	0.34	82.75
	ΣPAHs		73.18	66.45	8.63	335.02
	TSP		263.58	108.04	61.54	442.45

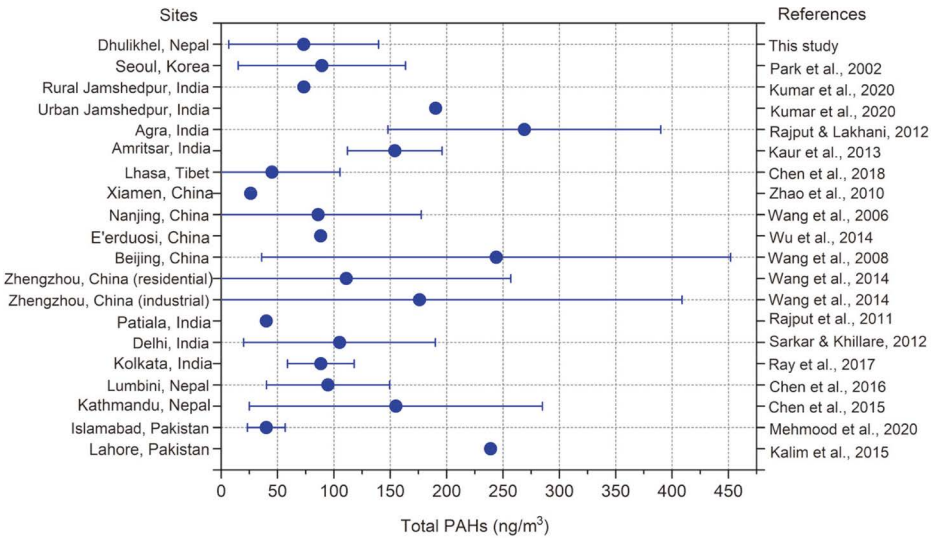

Fig. 2. Comparison of average concentrations (ng/m^3) of PAHs in Dhulikhel and other regions.

average TSP mass concentration during the study period was (264 ± 108 μg/m^3). TSP mass exhibited a reasonable correlation with PAH concentrations ($r = 0.46$; $p < 0.05$) in the study site as presented in Fig. S2, suggesting that PAH concentrations were dependent on aerosol particles. Previous studies on the chemical composition of ambient aerosols have suggested that anthropogenic emissions considerably influence the atmospheric composition in Dhulikhel via short and long-range pollutants transported from the Kathmandu valley and the IGP region (Bhattarai *et al.*, 2022; Tripathee *et al.*, 2021; Gautam *et al.*, 2011; Shrestha *et al.*, 2010). Such transported polluted air mass can have a significant impact on the atmospheric chemistry of the middle hill sites (Guo *et al.*, 2021).

Clear seasonality of the TSP and total PAHs concentrations was witnessed in the present study (Fig. 3). The higher concentrations of PAHs was found in the winter ranging from 42–170 with an average of 110 ng/m^3 followed by pre-monsoon ranging from 13–311 with an average of 72 ng/m^3 and lower concentration levels in the monsoon season ranging from 16–135 with an average of 42 ng/m^3. In addition, the K_{OA}-based approach was used to calculate the concentration of PAHs in the gas phase, which also exhibited clear variations seasonally with higher concentration levels in monsoon, and reduced to minimum concentrations in winter (Table 2). Generally, PAHs with two or three rings, having relatively lower log K_{OA} values, are mostly bound to the gaseous phase, PAHs with four rings are found in both the particle and gas phase, and PAHs with higher rings (five or more),

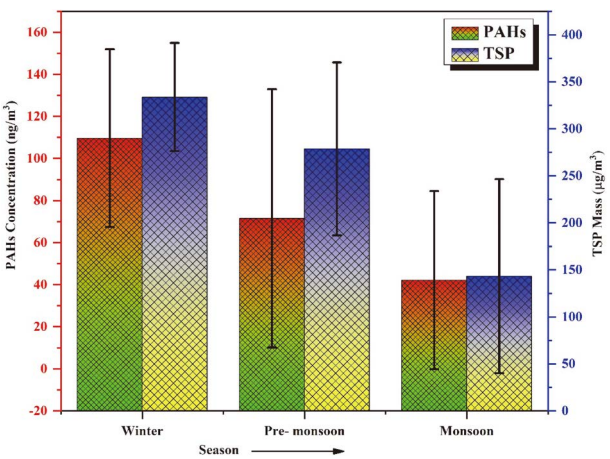

Fig. 3. Seasonal variations of TSP (μg/m^3) and PAH (ng/m^3) concentrations in the study site.

with higher log K_{OA} values, are present in the particulate phase. However, the temperature rise possibly increases the gas partitioning of PAHs with four or more rings. The PAH species with lower molecular weight, such as Flu, AcP, AcPy and Phe were the predominant compounds in the gas phase, whereas the higher molecular weight ones such as BghiP, IndP, BaP, BaF, Chr, BaA were found to be attached to particles and at higher concentrations than those in the gas phase. In addition, seasonal comparisons of PAH were performed by the Mann-Whitney Rank Sum Test using U-statistics due to the skewed distribution of the data. Statistically, PAH concentrations were significantly higher during the winter ($U = 9$, $n1 = 9$,

Table 2. Calculated gas-phase PAH concentrations (C_g) in the sampled seasons in the study site.

S.N	PAHs	Winter	Pre-monsoon	Monsoon
1	AcPy	2507.246	2270.5	3694.516
2	AcP	2616.039	3264.183	11175.449
3	Flu	1521.261	3864.065	22290.169
4	Phe	452.748	919.286	4745.825
5	AnT	97.814	125.471	355.263
6	FluA	76.207	92.532	189.353
7	Pyr	71.074	93.617	159.543
8	BaA	1.395	1.901	3.190
9	Chr	1.774	2.529	5.728
10	BbF	0.120	0.404	1.380
11	BkF	0.059	0.240	0.844
12	BaP	0.079	0.182	0.549
13	IndP	0.008	0.030	0.117
14	DbA	0.001	0.001	0.007
15	BghiP	0.007	0.027	0.091
	Total	7345.833	10634.968	42622.025

$n2 = 9$, $p < 0.05$) and pre-monsoon ($U = 67$, $n1 = 9$, $n2 = 30$, $p < 0.05$) compared to the monsoon season. In addition, winter-time PAH concentration was also significantly higher than that of the pre-monsoon season ($U = 56$, $n1 = 9$, $n2 = 30$, $p < 0.05$). It can be seen that the TSP mass concentration was higher to more than twice in winter than that in the monsoon period. Many previous studies have shown a similar seasonal trend of PAH levels (Kumar *et al.*, 2020; Mehmood *et al.*, 2020; Morakinyo *et al.*, 2019).

In the winter and pre-monsoon periods, the TSP mass and PAH concentrations were higher, suggesting high aerosol loads during the cold and dry seasons due to high emissions and less precipitation. Nevertheless, such weather conditions that promote the accumulation of air pollutants and atmospheric boundary layer heights are lower with stable atmospheric conditions and less dispersion of pollutants (Ram and Sarin, 2010). Further, the reduced photo-degradation and reduced volatility during lower temperature periods play an essential role in enhancing atmospheric pollutants (e.g., PAHs) during this period (Kaushal *et al.*, 2021; Elzein *et al.*, 2020). During the monsoon, low concentrations of particulate loading could be attributed to fewer pollution sources (e.g., brick kilns are not active and less biomass burning activities). In addition, the washing out of emitted contaminants by high precipitation during monsoon also dilutes the concentrations as shown in Supplementary figure (Fig. S3). The site is under the influence of large-scale pollutant transport from the IGP region as well as local sources around the Kathmandu valley (Shrestha *et al.*, 2010). Strong westerly winds during dry periods carry pollutants from the IGP region that can be transported over the Himalayan region. Intense biomass burning (BB) activities occur in the IGP region during dry periods causing intense haze over the region, which could have transported and deposited over the Himalayan region via long-range transport of atmospheric aerosols (Tripathee *et al.*, 2021; Rajput *et al.*, 2011; Ram and Sarin, 2010). The back trajectories of air-masses with satellite observations have been checked in a former study (Tripathee *et al.*, 2021), in the sampling site over different seasons. The results revealed that during the dry period (winter, pre-monsoon), the air masses from IGP and surrounding polluted regions reached the study site Dhulikhel, through atmospheric transport and that higher aerosol loads in those regions during dry periods were particularly caused by BB and other anthropogenic emissions. Such transported pollutants could have given rise to the high loadings of aerosol and particulate bound PAHs in our site during those periods. To further understand the influence of BB on PAH concentrations, we checked the correlations with BB tracer (nss-K^+) and shown in Supplementary figure (Fig. S4). The PAHs concentration was also positively correlated with nss-K^+ in winter ($r = 0.74$; $p < 0.05$) and pre-monsoon ($r = 0.57$; $p < 0.01$), (Fig. S4), supporting our assumption that BB could be a potentially crucial source of particulate PAHs in the dry periods over the study site.

3.2 PAH Compositions

The composition of PAHs is important for determining their potential sources of emission (Li *et al.*, 2017). 15 PAHs are classified into 4 groups on the aromatic ring number basis: including 3-ring PAHs (AcPy, AcP, Flu, PhA, and AnT), 4-ring PAHs (FluA, Pyr, BaA, and Chr), 5-ring PAHs (BbF, BkF, BaP, and DbA), and 6-ring PAHs (IndP and BghiP) (Kaur *et al.*, 2013). Lower molecular weight, LMW (3-rings) and middle molecular weight, MMW (4-rings) are more volatile than PAHs with higher molecular weight, HMW (5, 6-rings) and are partitioned between gaseous phase and particulate phase, which can be transported far and wide, even to the remote atmosphere. Generally, due to their low vapor pressures, most of the HMW PAHs are existent in the particulate phase

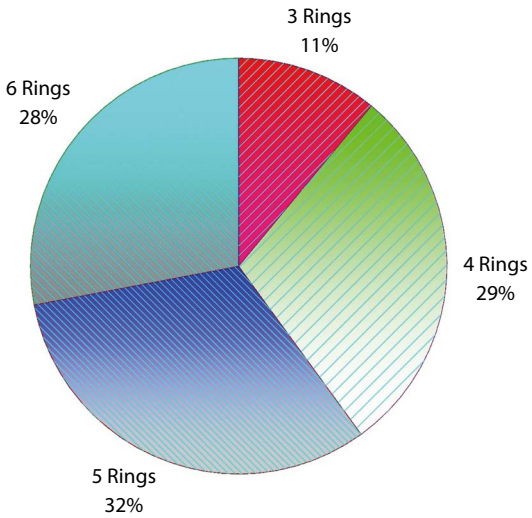

Fig. 4. Percentages of different ring PAHs in TSP in the study site.

and are adsorbed into fine particles. It has been found that 4-ring PAHs are released through coal combustion and BB, whereas 5- and 6-ring PAHs are mostly discharged from fuel processes with burning in high temperatures such as motor vehicular exhausts (Maharjan *et al.*, 2022; Chen *et al.*, 2018).

The composition of PAHs in Dhulikhel, Nepal, was predominated by 5-ring PAHs (32%), followed by 4-ring (29%) and 6-ring PAHs (28%). The 3-ring LMW PAHs constituted only 11% of the total PAHs in Dhulikhel (Fig. 4). This indicates that particle-bound PAHs result from petroleum combustion, such as vehicular emissions, followed by emissions from coal combustion origin and BB. The dominance of HMW PAHs shows that the sources have resulted from high-temperature courses, such as engine fuel burning (Tobiszewski and Namieśnik, 2012). A higher contribution of 4-ring PAHs suggests that there is a dominant influence of emission from fossil fuels (motor vehicle exhausts and coal combustion) (Chen *et al.*, 2015). The results are reasonable as our site is upwind of the polluted valley with numerous brick kiln emissions using low-grade coal and near to the Arniko highway with the frequent flow of heavy vehicles. Therefore, it indicates that most of the PAHs in our study site have originated from the local combustion of fossil fuel, including coal and BB, along with automobile exhausts.

3.3 PAHs Source Apportionment

To classify potential sources of atmospheric PAHs, characteristic molecular ratios and PCA approach were used.

3.3.1 Diagnostic Ratio Analysis

Anthropogenic activities, such as pyrogenic sources from partial combustion of organic materials like biomass, fossil fuels and emissions from petroleum products are the primary sources of atmospheric PAHs (Boonyatumanond *et al.*, 2006). Here, the PAH sources at Dhulikhel were recognized by comparing the ratios of selected PAHs. The ratios of Ant/(Ant + Phe), FluA/(FluA + Pyr), BaA/(BaA + Chr), IndP/(IndP + BghiP) and BaP/BghiP were calculated on a seasonal basis.

The Ant/(Ant + Phe) ratio value > 0.1 usually indicates the pyrogenic (combustion) origin, and < 0.1 indicates the petrogenic sources (Kamal *et al.*, 2014; Kong *et al.*, 2011; Budzinski *et al.*, 1997). In this study, most of the values exceeded 0.1, implying input from the pyrogenic origin in all winter, pre-monsoon and monsoon seasons. FluA/(FluA + Pyr) ratios are indicative of petrogenic source input, liquid fossil fuel combustion, or BB (Fang *et al.*, 2010; Mandalakis *et al.*, 2002; Rogge *et al.*, 1993). In the present study, most of the emissions were from petrogenic sources during the pre-monsoon and monsoon season, while emissions from liquid fossil fuel (petroleum) combustion, biomass, and coal-burning were prevalent in the winter season. Also, IndP/(IndP + BghiP) and BaA/(BaA + Chr) ratios are indicative of petrogenic and pyrogenic source input (Akyüz and Çabuk, 2010; Yunker *et al.*, 2002). In the current study, the ratio values of IndP/(IndP + BghiP) indicated emission from petroleum combustion and burning of coal, grass, and wood burning. Further, the ratio value of BaA/(BaA + Chr) was mostly greater than 0.2, indicating the existence of mixed sources (petroleum, biomass, and coal combustion). The BaP/BghiP ratio is considered an indicator of traffic and non-traffic sources, the values of which indicated the influence of traffic sources too in all the sampled seasons. The cross-plot analyses of diagnostic ratios are presented in Fig. 5. The analysis implies that the emissions of PAHs in the study site are from petrogenic as well as pyrogenic sources, particularly from petroleum combustion, coal and biomass burning, and automobile exhausts.

3.3.2 Principal Component Analysis (PCA)

The PCA was performed for investigation of the major sources of emissions of atmospheric PAHs in Dhulikhel, Nepal. A varimax rotation along with Kaiser Normalization was executed to identify the factors (Eigen value > 1). The results obtained are given in Table 3. Three prin-

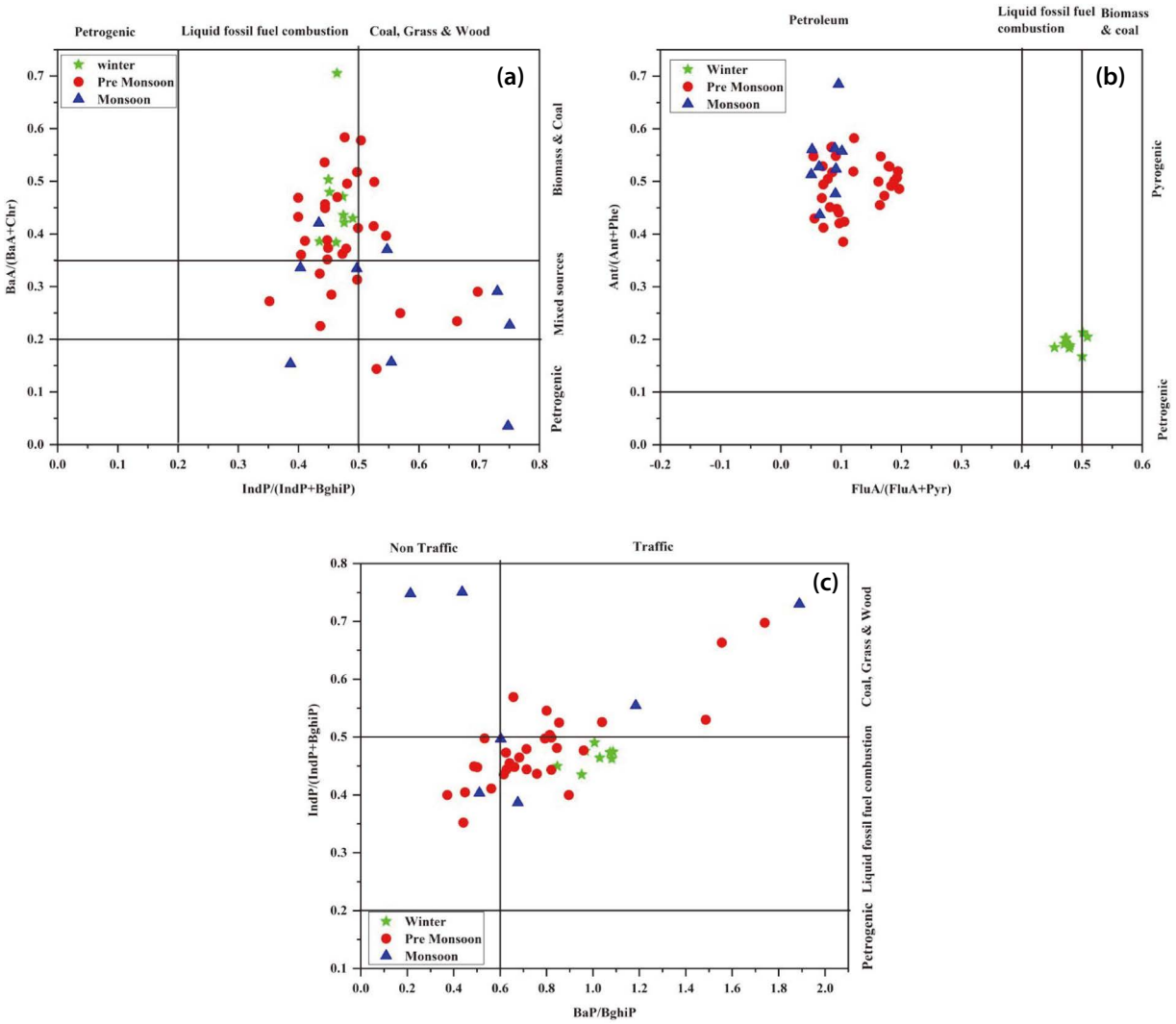

Fig. 5. The diagnostic ratios for source apportionment of PAHs.

cipal components (PCs) were obtained, accounting for 91% of the total variance.

PC-1 described 52.95% of the total variance and was found with FluA, Pyr, BaA, Chr, BaP, BbF, BkF, BghiP and IndP. Among these, FluA and Pyr are principally emitted from incomplete burning of coal, pyrolysis of fuel, and oil burning (Ravindra *et al.*, 2008; Harrison *et al.*, 1996). BaA and Chr are emitted from diesel and natural gas combustion (Khalili *et al.*, 1995). BaP, BbF, BkF, IndP and BghiP are reported as markers of vehicular emission by various studies (Fang *et al.*, 2010; Chang *et al.*, 2006; Park *et al.*, 2002; Simcik *et al.*, 1999; Harrison *et al.*, 1996). Therefore, PC-1 represented the contribution of combustion of fossil fuel sources. PC-2 accounted for about 29% of total variability and loaded highly on LMW PAHs like AcPy, AcP, Phe and AnT, which could be identified as combustion origin (coal) (Wang *et al.*, 2008; Mastral *et al.*, 1996). PC-3 showed a variance of 9% and was loaded with Flu and Phe. Therefore, the PCA results showed that the study area was affected by diverse sources of fossil fuel combustion and vehicular emissions.

3.4 Health Risk Assessment

Carcinogenic human health risks from the atmospheric PAHs through inhalation of air particles and possible health risk implications were assessed. The health risk estimation was done by determining the values of total BaP_{eq}, LLCR, and ILCR in Dhulikhel over the sampling

Table 3. Principal component analysis in the study site.

PAHs	PC-1 (Variance - 52.95%)	PC-2 (Variance - 29.19%)	PC-3 (Variance - 8.97%)
AcPy	0.143	0.411	−0.081
AcP	0.096	0.437	0.065
Flu	−0.123	0.017	0.763
Phe	0.079	0.313	0.559
AnT	0.156	0.405	−0.038
FluA	0.328	0.095	-4.80×10^{-4}
Pyr	0.339	0.008	0.036
BaA	0.328	0.138	−0.081
Chr	0.330	0.036	−0.061
BbF	0.292	−0.248	0.039
BkF	0.264	−0.289	0.098
BaP	0.331	−0.150	0.043
IndP	0.290	−0.250	0.120
DbA	0.238	0.251	−0.161
BghiP	0.283	−0.236	0.167

periods. The total BaP_{eq} of 15 PAHs during the sampling period was found to vary from 1.26 to 51.49 ng/m^3, having a mean value of 11.71 ng/m^3, indicating the likely adverse health risks for local inhabitants (Table 4). This value exceeded the standard (1 ng/m^3) as given by the WHO guideline and European Commission (EC) (WHO, 2000; Chen *et al.*, 2017b). BaP alone contributed to about 67% carcinogenicity of the total PAHs in the study site.

The average LLCR was calculated for Dhulikhel as 1.01×10^{-3}, which was above the standard cancer risk level, as the upper limit of LLCR values specified by USEPA and the EC is $< 10^{-6}$ to 10^{-4} per year (Jamhari *et al.*, 2014). Furthermore, the health risk assessment was performed by calculating the LADD values of PAHs for the age-specific group (adults and children) and then estimating their associated values of ILCR. According to most of the regulatory standard programs, the ILCR value between 10^{-6} to 10^{-4} specifies potential cancer risks, representing the rise in cancer chance by one in a million people, whereas an ILCR value exceeding 10^{-4} is considered as significant cancer risk and an ILCR value of $< 10^{-4}$ represents negligible risks of cancer (Chen and Liao, 2006; USEPA, 1989). The average ILCR associated with carcinogenic PAHs in Dhulikhel was estimated to be 8.78×10^{-6} for adults and 2.47×10^{-5} for children, respectively. The ILCR value obtained in this study for adults suggests that it falls under the potential risk of cancer. This value is comparable to the average ILCR value

Table 4. Values of TEF for individual PAHs, mean concentrations of PAHs and BaP_{eq} (ng/m^3) in the study site.

PAHs	TEF[a]	Mean PAH (ng/m^3)	BaP_{eq} (ng/m^3)	BaP_{eq} (%)
AcPy	0.001	0.38	0.0004	0.003
AcP	0.001	0.81	0.001	0.007
Flu	0.001	2.29	0.002	0.020
Phe	0.001	3.67	0.004	0.031
AnT	0.01	0.57	0.006	0.048
FluA	0.001	5.30	0.005	0.045
Pyr	0.001	5.91	0.006	0.050
BaA	0.1	4.30	0.430	3.672
Chr	0.01	5.96	0.060	0.509
BbF	0.1	9.27	0.927	7.917
BkF	0.1	5.76	0.576	4.922
BaP	1	7.82	7.817	66.751
IndP	0.1	9.49	0.949	8.100
DbA	1	0.82	0.819	6.997
BghiP	0.01	10.84	0.108	0.926
Total		73.18	11.71	

[a]TEF: Toxicity equivalency factors adopted (Nisbet and Lagoy, 1992)

of Lumbini, Nepal (7.10×10^{-6}), and Jamshedpur, India (15.78×10^{-6}) (Kumar *et al.*, 2020), but lower than that obtained in the urban cities, Kathmandu, Nepal (1.04×10^{-5}) (Neupane *et al.*, 2018) and Amritsar, India 72×10^{-5} (Kaur *et al.*, 2013). On the contrary, the average ILCR value obtained in the study site for children suggests that the cancer risk level in this site is very high, and the adverse consequences of carcinogenic PAHs on children's health are more serious. These results indicate the need for attention to mitigate the emissions from contributors of total carcinogenic potential to reduce the adverse human health risks from inhalation of airborne PAHs.

4. CONCLUSIONS

This study offers the measurements of concentrations, seasonality and evaluates the sources and health risk assessment of particle-bound PAHs in ambient aerosols from January to July 2018 in Dhulikhel, a middle hill region of the Central Himalayas. The average levels of TSP (264 ± 108 μg/m^3) and PAHs (73 ± 66 ng/m^3) obtained exhibited similarity with those of some South-Asian cities. Evident seasonal variation of total PAHs was observed with higher levels during the dry season (pre-monsoon and winter) than those in the wet period (mon-

soon), attributed to higher emission sources and less dispersion during dry periods. The dominant species was 5-ring PAHs (32%), followed by 4-ring (29%) and 6-ring PAHs (28%).

Source apportionment using diagnostic ratios and PCA revealed mixed sources of emission like petrogenic as well as pyrogenic sources, particularly from fossil fuel combustion, biomass burning, and automobile exhausts to be the possible pollution sources in the site. Anthropogenic emissions from surrounding polluted areas and the IGP region could be responsible for particulate loading in the Himalayas. The mean total BaP_{eq} level of PAHs in Dhulikhel was 11.71 ng/m^3, signifying the potential adverse health risks for local inhabitants. The average ILCR associated with carcinogenic PAHs was estimated to be 8.78×10^{-6} for adults, indicating the potential risk of cancer and 2.47×10^{-5} for children, indicating serious carcinogenic effects of PAHs on children's health. This study delivers the first dataset of PAHs in the Himalayan middle hills, which is essential to formulate control strategies to reduce atmospheric emissions and health threats owing to PAHs over the region.

ACKNOWLEDGEMENT

The Pan-Third Pole Environment Study for a Green Silk Road (Pan-TPE) (XDA20040501), National Natural Science Foundation of China (41705132, 41630754), CAS "Light of West China" program and the State Key Laboratory of Cryospheric Science (SKLCS-OP-2018-01) supported this study. Dr. Lekhendra Tripathee is thankful to the Asia-Pacific Network for Global Change Research (APN) for the grant (Grant reference: CRECS 2020-07MYTripathee) and Chinese Academy of Sciences for providing President's International Fellowship Initiative (PIFI) as Young Staff (2020FYC0001). This study is part of the research initiative: Atmospheric Pollution and Cryospheric Change (APCC). The authors would like to express their deep gratitude towards Bhaskar Shrestha for the help and support.

REFERENCES

Akyüz, M., Çabuk, H. (2010) Gas-particle partitioning and seasonal variation of polycyclic aromatic hydrocarbons in the atmosphere of Zonguldak, Turkey. Science of the total Environment, 408(22), 5550–5558. https://doi.org/10.1016/j.scitotenv.2010.07.063

Ayyildiz, E.G., Esen, F. (2020) Atmospheric polycyclic aromatic hydrocarbons (PAHs) at two sites, in Bursa, Turkey: determination of concentrations, gas-particle partitioning, sources, and health risk. Archives of Environmental Contamination and Toxicology, 78, 350–366. https://doi.org/10.1007/s00244-019-00698-7

Bhattarai, H., Tripathee, L., Kang, S., Chen, P., Sharma, C.M., Ram, K., Rupakheti, M. (2022) Nitrogenous and carbonaceous aerosols in $PM_{2.5}$ and TSP during pre-monsoon: Characteristics and sources in the highly polluted mountain valley. Journal of Environmental Sciences, 115, 10–24. https://doi.org/10.1016/j.jes.2021.06.018

Bi, X., Luo, W., Gao, J., Xu, L., Guo, J., Zhang, Q., Romesh, K.Y., Giesy, J.P., Kang, S., de Boer, J. (2016) Polycyclic aromatic hydrocarbons in soils from the Central-Himalaya region: Distribution, sources, and risks to humans and wildlife. Science of The Total Environment, 556, 12–22. https://doi.org/10.1016/j.scitotenv.2016.03.006

Boonyatumanond, R., Wattayakorn, G., Togo, A., Takada, H. (2006) Distribution and origins of polycyclic aromatic hydrocarbons (PAHs) in riverine, estuarine, and marine sediments in Thailand. Marine Pollution Bulletin, 52(8), 942–956. https://doi.org/10.1016/j.marpolbul.2005.12.015

Bortey-Sam, N., Ikenaka, Y., Akoto, O., Nakayama, S.M., Yohannes, Y.B., Baidoo, E., Mizukawa, H., Ishizuka, M. (2015) Levels, potential sources and human health risk of polycyclic aromatic hydrocarbons (PAHs) in particulate matter (PM_{10}) in Kumasi, Ghana. Environmental Science and Pollution Research, 22(13), 9658–9667. https://doi.org/10.1007/s11356-014-4022-1

Budzinski, H., Jones, I., Bellocq, J., Pierard, C., Garrigues, P. (1997) Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. Marine Chemistry, 58(1–2), 85–97. https://doi.org/10.1016/S0304-4203(97)00028-5

Chang, K.-F., Fang, G.-C., Chen, J.-C., Wu, Y.-S. (2006) Atmospheric polycyclic aromatic hydrocarbons (PAHs) in Asia: a review from 1999 to 2004. Environmental Pollution, 142(3), 388–396. https://doi.org/10.1016/j.envpol.2005.09.025

Chen, P., Kang, S., Li, C., Li, Q., Yan, F., Guo, J., Ji, Z., Zhang, Q., Hu, Z., Tripathee, L., Sillanpää, M. (2018) Source Apportionment and Risk Assessment of Atmospheric Polycyclic Aromatic Hydrocarbons in Lhasa, Tibet, China. Aerosol and Air Quality Research, 18(5), 1294–1304. https://doi.org/10.4209/aaqr.2017.12.0603

Chen, P., Kang, S., Li, C., Rupakheti, M., Yan, F., Li, Q., Ji, Z., Zhang, Q., Luo, W., Sillanpää, M. (2015) Characteristics and sources of polycyclic aromatic hydrocarbons in atmospheric aerosols in the Kathmandu Valley. Nepal. Science of the Total Environment, 538, 86–92. https://doi.org/10.1016/j.scitotenv.2015.08.006

Chen, P., Kang, S., Li, C., Zhang, Q., Guo, J., Tripathee, L., Zhang, Y., Li, G., Gul, C., Cong, Z., Wan, X. (2019) Carbonaceous aerosol characteristics on the Third Pole: A primary study based on the Atmospheric Pollution and Cryospheric Change (APCC) network. Environmental Pollution, 253,

49–60. https://doi.org/10.1016/j.envpol.2019.06.112
Chen, P., Kang, S., Tripathee, L., Panday, A.K., Rupakheti, M., Rupakheti, D., Zhang, Q., Guo, J., Li, C., Pu, T. (2020) Severe air pollution and characteristics of light-absorbing particles in a typical rural area of the Indo-Gangetic Plain. Environmental Science and Pollution Research, 27, 10617–10628. https://doi.org/10.1007/s11356-020-07618-6
Chen, P., Li, C., Kang, S., Rupakheti, M., Panday, A.K., Yan, F., Li, Q., Zhang, Q., Guo, J., Ji, Z., Rupakheti, D. (2017) Characteristics of Particulate-Phase Polycyclic Aromatic Hydrocarbons (PAHs) in the Atmosphere over the Central Himalayas. Aerosol and Air Quality Research, 17(12), 2942–2954. https://doi.org/10.4209/aaqr.2016.09.0385
Chen, P., Li, C., Kang, S., Yan, F., Zhang, Q., Ji, Z., Tripathee, L., Rupakheti, D., Rupakheti, M., Qu, B., Sillanpää, M. (2016) Source apportionment of particle-bound polycyclic aromatic hydrocarbons in Lumbini, Nepal by using the positive matrix factorization receptor model. Atmospheric Research, 182, 46–53. https://doi.org/10.1016/j.atmosres.2016.07.011
Chen, S.-C., Liao, C.-M. (2006) Health risk assessment on human exposed to environmental polycyclic aromatic hydrocarbons pollution sources. Science of The Total Environment, 366(1), 112–123. https://doi.org/10.1016/j.scitotenv.2005.08.047
Chen, Y., Li, X., Zhu, T., Han, Y., Lv, D. (2017) $PM_{2.5}$-bound PAHs in three indoor and one outdoor air in Beijing: Concentration, source and health risk assessment. Science of The Total Environment, 586, 255–264. https://doi.org/10.1016/j.scitotenv.2017.01.214
Conde, F.J., Ayala, J.H., Afonso, A.M., González, V. (2005) Emissions of polycyclic aromatic hydrocarbons from combustion of agricultural and sylvicultural debris. Atmospheric Environment, 39(35), 6654–6663. https://doi.org/10.1016/j.atmosenv.2005.07.043
Elzein, A., Stewart, G.J., Swift, S.J., Nelson, B.S., Crilley, L.R., Alam, M.S., Reyes-Villegas, E., Gadi, R., Harrison, R.M., Hamilton, J.F., Lewis, A.C. (2020) A comparison of $PM_{2.5}$-bound polycyclic aromatic hydrocarbons in summer Beijing (China) and Delhi (India). Atmospheric Chemistry and Physics, 20(22), 14303–14319. https://doi.org/10.5194/acp-20-14303-2020
Esen, F., Tasdemir, Y., Bozkurt, Y.M. (2019) Assessments of seasonal trend, gas-particle partitioning and deposition flux of polycyclic aromatic hydrocarbons at a semi-rural site. Journal of Environmental Science and Health, Part A, 54(6), 582–591. https://doi.org/10.1080/10934529.2019.1574158
Fang, G.-C., Huang, J.-H., Huang, Y.-L. (2010) Polycyclic aromatic hydrocarbon pollutants in the Asian atmosphere during 2001 to 2009. Environmental Forensics, 11(3), 207–215. https://doi.org/10.1080/15275922.2010.495934
Gaga, E.O., Ari, A., Döğeroğlu, T., Çakırca, E.E., Machin, N.E. (2012) Atmospheric polycyclic aromatic hydrocarbons in an industrialized city, Kocaeli, Turkey: study of seasonal variations, influence of meteorological parameters and health risk estimation. Journal of Environmental Monitoring, 14(8), 2219–2229. https://doi.org/10.1039/C2EM30118K
Gautam, R., Hsu, N.C., Tsay, S.C., Lau, K.M., Holben, B., Bell, S., Smirnov, A., Li, C., Hansell, R., Ji, Q., Payra, S. (2011) Accumulation of aerosols over the Indo-Gangetic plains and southern slopes of the Himalayas: distribution, properties and radiative effects during the 2009 pre-monsoon season. Atmospheric Chemistry and Physics, 11(24), 12841–12863. https://doi.org/10.5194/acp-11-12841-2011
Guo, J., Kang, S., Huang, J., Zhang, Q., Rupakheti, M., Sun, S., Tripathee, L., Rupakheti, D., Panday, A.K., Sillanpää, M., Paudyal, R. (2017) Characterizations of atmospheric particulate-bound mercury in the Kathmandu Valley of Nepal, South Asia. Science of the Total Environment, 579, 1240–1248. https://doi.org/10.1016/j.scitotenv.2016.11.110
Guo, J., Ram, K., Tripathee, L., Kang, S., Huang, J., Chen, P., Ghimire, P.S. (2020) Study on Mercury in PM_{10} at an Urban Site in the Central Indo-Gangetic Plain: Seasonal Variability and Influencing Factors. Aerosol and Air Quality Research, 20, 2729–2740. https://doi.org/10.4209/aaqr.2019.12.0630
Guo, J., Sharma, C.M., Tripathee, L., Kang, S., Fu, X., Huang, J., Shrestha, K.L., Chen, P. (2021) Source identification of atmospheric particle-bound mercury in the Himalayan foothills through non-isotopic and isotope analyses. Environmental Pollution, 286, 117317. https://doi.org/10.1016/j.envpol.2021.117317
Guo, J., Tripathee, L., Kang, S., Zhang, Q., Huang, J., Sharma, C.M., Chen, P., Paudyal, R., Rupakheti, D. (2022) Atmospheric particle-bound mercury in the northern Indo-Gangetic Plain region: Insights into sources from mercury isotope analysis and influencing factors. Geoscience Frontiers, 13(1), 101274. https://doi.org/10.1016/j.gsf.2021.101274
Harner, T., Bidleman, T.F. (1996) Measurements of octanol - air partition coefficients for polychlorinated biphenyls. Journal of Chemical & Engineering Data, 41(4), 895–899. https://doi.org/10.1021/je960097y
Harner, T., Bidleman, T.F. (1998) Octanol - air partition coefficient for describing particle/gas partitioning of aromatic compounds in urban air. Environmental Science & Technology, 32(10), 1494–1502. https://doi.org/10.1021/es970890r
Harrison, R.M., Smith, D., Luhana, L. (1996) Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK. Environmental Science & Technology, 30(3), 825–832. https://doi.org/10.1021/es950252d
IARC (International Agency for Research on Cancer) (2010) Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures. IARC Monographs on the evaluation of carcinogenic risks to humans, 92, 1.
Jamhari, A.A., Sahani, M., Latif, M.T., Chan, K.M., Tan, H.S., Khan, M.F., Tahir, N.M. (2014) Concentration and source identification of polycyclic aromatic hydrocarbons (PAHs) in PM_{10} of urban, industrial and semi-urban areas in Malaysia. Atmospheric Environment, 86, 16–27. https://doi.org/10.1016/j.atmosenv.2013.12.019
Juhasz, A.L., Naidu, R. (2000) Bioremediation of high molecular weight polycyclic aromatic hydrocarbons: a review of the microbial degradation of benzo[a]pyrene. International Biodeterioration & Biodegradation, 45(1–2), 57–88. https://doi.org/10.1016/S0964-8305(00)00052-4

Kamal, A., Cincinelli, A., Martellini, T., Malik, R.N. (2015) A review of PAH exposure from the combustion of biomass fuel and their less surveyed effect on the blood parameters. Environmental Science and Pollution Research, 22(6), 4076–4098. https://doi.org/10.1007/s11356-014-3748-0

Kamal, A., Malik, R.N., Martellini, T., Cincinelli, A. (2014) Cancer risk evaluation of brick kiln workers exposed to dust bound PAHs in Punjab province (Pakistan). Science of The Total Environment, 493, 562–570. https://doi.org/10.1016/j.scitotenv.2014.05.140

Kang, S., Zhang, Q., Qian, Y., Ji, Z., Li, C., Cong, Z., Zhang, Y., Guo, J., Du, W., Huang, J., You, Q., Qin, D. (2019) Linking Atmospheric Pollution to Cryospheric Change in the Third Pole Region: Current Progresses and Future Prospects. National Science Review, 6, 796–809. https://doi.org/10.1093/nsr/nwz031

Kaur, S., Senthilkumar, K., Verma, V.K., Kumar, B., Kumar, S., Katnoria, J.K. Sharma, C.S. (2013) Preliminary Analysis of Polycyclic Aromatic Hydrocarbons in Air Particles (PM_{10}) in Amritsar, India: Sources, Apportionment, and Possible Risk Implications to Humans. Archives of Environmental Contamination and Toxicology, 65(3), 382–395. https://doi.org/10.1007/s00244-013-9912-6

Kaushal, D., Bamotra, S., Yadav, S., Chatterjee, S., Tandon, A. (2021) Particulate bound polycyclic aromatic hydrocarbons over Dhauladhar region of the north-western Himalayas. Chemosphere, 263, 128298. https://doi.org/10.1016/j.chemosphere.2020.128298

Khalili, N.R., Scheff, P.A., Holsen, T.M. (1995) PAH source fingerprints for coke ovens, diesel and, gasoline engines, highway tunnels, and wood combustion emissions. Atmospheric Environment, 29(4), 533–542. https://doi.org/10.1016/1352-2310(94)00275-P

Kim, K.-H., Jahan, S.A., Kabir, E., Brown, R.J. (2013) A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects. Environment International, 60, 71–80. https://doi.org/10.1016/j.envint.2013.07.019

Kong, S., Shi, J., Lu, B., Qiu, W., Zhang, B., Peng, Y., Zhang, B., Bai, Z. (2011) Characterization of PAHs within PM_{10} fraction for ashes from coke production, iron smelt, heating station and power plant stacks in Liaoning Province, China. Atmospheric Environment, 45(23), 3777–3785. https://doi.org/10.1016/j.atmosenv.2011.04.029

Kumar, A., Ambade, B., Sankar, T.K., Sethi, S.S., Kurwadkar, S. (2020) Source identification and health risk assessment of atmospheric $PM_{2.5}$-bound polycyclic aromatic hydrocarbons in Jamshedpur, India. Sustainable Cities and Society, 52, 101801. https://doi.org/10.1016/j.scs.2019.101801

Lee, S., Ho, K., Chan, L., Zielinska, B., Chow, J.C. (2001) Polycyclic aromatic hydrocarbons (PAHs) and carbonyl compounds in urban atmosphere of Hong Kong. Atmospheric Environment, 35(34), 5949–5960. https://doi.org/10.1016/S1352-2310(01)00374-0

Li, Q., Kang, S., Wang, N., Li, Y., Li, X., Dong, Z., Chen, P. (2017) Composition and sources of polycyclic aromatic hydrocarbons in cryoconites of the Tibetan Plateau glaciers. Science of The Total Environment, 574, 991–999. https://doi.org/10.1016/j.scitotenv.2016.09.159

Maharjan, L., Kang, S., Tripathee, L., Gul, C., Zheng, H., Li, Q., Chen, P., Rai, M., Santos, E. (2022) Atmospheric particle-bound polycyclic aromatic compounds over two distinct sites in Pakistan: Characteristics, sources and health risk assessment. Journal of Environmental Sciences, 112, 1–15. https://doi.org/10.1016/j.jes.2021.04.024

Mandalakis, M., Tsapakis, M., Tsoga, A., Stephanou, E.G. (2002) Gas-particle concentrations and distribution of aliphatic hydrocarbons, PAHs, PCBs and PCDD/Fs in the atmosphere of Athens (Greece). Atmospheric Environment, 36(25), 4023–4035. https://doi.org/10.1016/S1352-2310(02)00362-X

Mastral, A.M., Callen, M., Murillo, R. (1996) Assessment of PAH emissions as a function of coal combustion variables. Fuel, 75(13), 1533–1536. https://doi.org/10.1016/0016-2361(96)00120-2

Mehmood, T., Zhu, T., Ahmad, I., Li, X. (2020) Ambient $PM_{2.5}$ and PM_{10} bound PAHs in Islamabad, Pakistan: Concentration, source and health risk assessment. Chemosphere, 257, 127187. https://doi.org/10.1016/j.chemosphere.2020.127187

Morakinyo, O.M., Mukhola, M.S., Mokgobu, M.I. (2020) Concentration levels and carcinogenic and mutagenic risks of $PM_{2.5}$-bound polycyclic aromatic hydrocarbons in an urban-industrial area in South Africa. Environmental Geochemistry and Health, 42, 2163–2178. https://doi.org/10.1007/s10653-019-00493-2

Neupane, B., Chen, P., Kang, S., Tripathee, L., Rupakheti, D., Sharma, C.M. (2018) Health risk assessment of atmospheric polycyclic aromatic hydrocarbons over the Central Himalayas. Human and Ecological Risk Assessment: An International Journal, 24(7), 1969–1982. https://doi.org/10.1080/10807039.2018.1435254

Nisbet, I.C., Lagoy, P.K. (1992) Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Regulatory Toxicology and Pharmacology, 16(3), 290–300. https://doi.org/10.1016/0273-2300(92)90009-X

Odabasi, M., Cetin, E., Sofuoglu, A. (2006) Determination of octanol - air partition coefficients and supercooled liquid vapor pressures of PAHs as a function of temperature: application to gas-particle partitioning in an urban atmosphere. Atmospheric Environment, 40(34), 6615–6625. https://doi.org/10.1016/j.atmosenv.2006.05.051

Park, S.S., Kim, Y.J., Kang, C.H. (2002) Atmospheric polycyclic aromatic hydrocarbons in Seoul, Korea. Atmospheric Environment, 36(17), 2917–2924. https://doi.org/10.1016/S1352-2310(02)00206-6

Rajput, N., Lakhani, A. (2012) Particle Associated Polycyclic Aromatic Hydrocarbons (PAHS) in Urban Air of Agra. Polycyclic Aromatic Compounds, 32(1), 48–60. https://doi.org/10.1080/10406630903299520

Rajput, P., Sarin, M.M., Rengarajan, R., Singh, D. (2011) Atmospheric polycyclic aromatic hydrocarbons (PAHs) from post-harvest biomass burning emissions in the Indo-Gangetic Plain: Isomer ratios and temporal trends. Atmospheric Environment, 45(37), 6732–6740. https://doi.org/10.1016/j.atmosenv.2011.08.018

Rajput, P., Sarin, M.M., Sharma, D., Singh, D. (2014) Atmo-

spheric polycyclic aromatic hydrocarbons and isomer ratios as tracers of biomass burning emissions in Northern India. Environmental Science and Pollution Research, 21(8), 5724–5729. https://doi.org/10.1007/s11356-014-2496-5

Ram, K., Sarin, M. (2010) Spatio-temporal variability in atmospheric abundances of EC, OC and WSOC over Northern India. Journal of Aerosol Science, 41(1), 88–98. https://doi.org/10.1016/j.jaerosci.2009.11.004

Ravindra, K., Sokhi, R., Van Grieken, R. (2008) Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmospheric Environment, 42(13), 2895–2921. https://doi.org/10.1016/j.atmosenv.2007.12.010

Ray, D., Chatterjee, A., Majumdar, D., Ghosh, S.K., Raha, S. (2017) Polycyclic aromatic hydrocarbons over a tropical urban and a high altitude Himalayan Station in India: temporal variation and source apportionment. Atmospheric Research, 197, 331–341. https://doi.org/10.1016/j.atmosres.2017.07.010

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R. (1993) Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. Environmental Science & Technology, 27(4), 636–651. https://doi.org/10.1021/es00041a007

Sarkar, S., Khillare, P.S. (2012) Profile of PAHs in the inhalable particulate fraction: source apportionment and associated health risks in a tropical megacity. Environmental Monitoring and Assessment, 185(2), 1199–1213. https://doi.org/10.1007/s10661-012-2626-9

Shrestha, P., Barros, A.P., Khlystov, A. (2010) Chemical composition and aerosol size distribution of the middle mountain range in the Nepal Himalayas during the 2009 pre-monsoon season. Atmospheric Chemistry and Physics, 10(23), 11605–11621. https://doi.org/10.5194/acp-10-11605-2010

Simcik, M.F., Eisenreich, S.J., Lioy, P.J. (1999) Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. Atmospheric Environment, 33(30), 5071–5079. https://doi.org/10.1016/S1352-2310(99)00233-2

Singh, D.P., Gadi, R., Mandal, T.K., Saud, T., Saxena, M., Sharma, S.K. (2013) Emissions estimates of PAH from biomass fuels used in rural sector of Indo-Gangetic Plains of India. Atmospheric Environment, 68, 120–126. https://doi.org/10.1016/j.atmosenv.2012.11.042

Suvarapu, L.N., Seo, Y.-K., Lee, B.-S., Baek, S.-O. (2012) A review on the atmospheric concentrations of polycyclic aromatic hydrocarbons (PAHs) in Asia since 2000 - part I: data from developed countries. Asian Journal of Atmospheric Environment, 6(3), 147–168. https://doi.org/10.5572/ajae.2012.6.3.147

Tobiszewski, M., Namieśnik, J. (2012) PAH diagnostic ratios for the identification of pollution emission sources. Environmental Pollution, 162, 110–119. https://doi.org/10.1016/j.envpol.2011.10.025

Tripathee, L., Guo, J., Kang, S., Paudyal, R., Huang, J., Sharma, C.M., Zhang, Q., Chen, P., Ghimire, P.S., Sigdel, M. (2019) Spatial and temporal distribution of total mercury in atmospheric wet precipitation at four sites from the Nepal-Himalayas. Science of The Total Environment, 655, 1207–1217. https://doi.org/10.1016/j.scitotenv.2018.11.338

Tripathee, L., Kang, S., Chen, P., Bhattarai, H., Guo, J., Shrestha, K.L., Sharma, C.M., Ghimire, P.S., Huang, J. (2021) Water-soluble organic and inorganic nitrogen in ambient aerosols over the Himalayan middle hills: Seasonality, sources, and transport pathways. Atmospheric Research, 250, 105376. https://doi.org/10.1016/j.atmosres.2020.105376

Tripathee, L., Kang, S., Rupakheti, D., Cong, Z., Zhang, Q., Huang, J. (2017) Chemical characteristics of soluble aerosols over the central Himalayas: insights into spatiotemporal variations and sources. Environmental Science and Pollution Research, 24(31), 24454–24472. https://doi.org/10.1007/s11356-017-0077-0

Tripathee, L., Kang, S., Rupakheti, D., Zhang, Q., Huang, J., Sillanpää, M. (2016) Water-Soluble Ionic Composition of Aerosols at Urban Location in the Foothills of Himalaya, Pokhara Valley, Nepal. Atmosphere, 7(8), 102. https://doi.org/10.3390/atmos7080102

USEPA (United States Environmental Protection Agency) (1989) Risk assessment guidance for superfund. Human Health Evaluation Manual Part A.

USEPA (United States Environmental Protection Agency) (2011) Exposure Factors Handbook 2011 Edition (Final Report). US Environmental Protection Agency, Washington, DC, EPA/600/R-09/052F.

Verma, P.K., Sah, D., Kumari, K.M., Lakhani, A. (2017) Atmospheric concentrations and gas-particle partitioning of polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs at Indo-Gangetic sites. Environmental Science: Processes & Impacts, 19(8), 1051–1060. https://doi.org/10.1039/C7EM00168A

Wang, G., Huang, L., Zhao, X., Niu, H., Dai, Z. (2006) Aliphatic and polycyclic aromatic hydrocarbons of atmospheric aerosols in five locations of Nanjing urban area, China. Atmospheric Research, 81(1), 54–66. https://doi.org/10.1016/j.atmosres.2005.11.004

Wang, X., Cheng, H., Xu, X., Zhuang, G., Zhao, C. (2008) A wintertime study of polycyclic aromatic hydrocarbons in $PM_{2.5}$ and $PM_{2.5-10}$ in Beijing: assessment of energy structure conversion. Journal of Hazardous Materials, 157(1), 47–56. https://doi.org/10.1016/j.jhazmat.2007.12.092

Wang, Z., Na, G., Ma, X., Fang, X., Ge, L., Gao, H., Yao, Z. (2013) Occurrence and gas/particle partitioning of PAHs in the atmosphere from the North Pacific to the Arctic Ocean. Atmospheric Environment, 77, 640–646. https://doi.org/10.1016/j.atmosenv.2013.05.052

WHO (World Health Organization) (2000) Air quality guidelines for Europe.

Wu, D., Wang, Z., Chen, J., Kong, S., Fu, X., Deng, H., Shao, G., Wu, G. (2014) Polycyclic aromatic hydrocarbons (PAHs) in atmospheric $PM_{2.5}$ and PM_{10} at a coal-based industrial city: Implication for PAH control at industrial agglomeration regions, China. Atmospheric Research, 149, 217–229. https://doi.org/10.1016/j.atmosres.2014.06.012

Yang, J., Xu, W., Cheng, H. (2018) Seasonal variations and sources of airborne polycyclic aromatic hydrocarbons (PAHs) in

Chengdu, China. Atmosphere, 9(2), 63. https://doi.org/10.3390/atmos9020063
Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S. (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Organic Geochemistry, 33(4), 489–515. https://doi.org/10.1016/S0146-6380(02)00002-5
Zhang, Q., Zhang, F., Kang, S., Cong, Z. (2017) Melting glaciers: Hidden hazards. Science, 356(6337), 495. https://doi.org/10.1126/science.aan4118
Zhang, Y., Tao, S. (2009) Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004. Atmospheric Environment, 43(4), 812–819. https://doi.org/10.1016/j.atmosenv.2008.10.050
Zhu, X., Pfister, G., Henkelmann, B., Kotalik, J., Bernhöft, S., Fiedler, S., Schramm, K.W. (2008) Simultaneous monitoring of profiles of polycyclic aromatic hydrocarbons in contaminated air with semipermeable membrane devices and spruce needles. Environmental Pollution, 156(2), 461–466. https://doi.org/10.1016/j.envpol.2008.01.023

SUPPLEMENTARY MATERIALS

Table S1. Parameters of equation (1) and octanol-air partition coefficients (K_{OA}) of PAHs at 10°C, 18°C, and 23°C in winter, pre-monsoon and monsoon season, respectively.

S.N	PAHs	A	B	log K_{OA} (10°C)	log K_{OA} (18°C)	log K_{OA} (23°C)
1	AcPy[b]	−1.97	2476	6.77	6.53	6.39
2	AcP[b]	−2.20	2597	6.97	6.72	6.57
3	Flu[a]	−2.61	2833	7.40	7.12	6.96
4	Phe[a]	−3.37	3293	8.26	7.94	7.75
5	AnT[b]	−3.41	3316	8.30	7.98	7.79
6	FluA[a]	−4.34	3904	9.45	9.07	8.84
7	Pyr[a]	−4.56	3985	9.51	9.13	8.90
8	BaA[b]	−5.64	4746	11.12	10.66	10.39
9	Chr[b]	−5.65	4754	11.14	10.68	10.40
10	BbF[b]	−6.40	5285	12.27	11.75	11.45
11	BkF[b]	−6.42	5301	12.30	11.79	11.48
12	BaP[b]	−6.50	5382	12.51	11.99	11.67
13	IndP[b]	−7.00	5791	13.45	12.89	12.55
14	DbA[b]	−7.17	5887	13.62	13.05	12.71
15	BghiP[b]	−7.03	5834	13.57	13.01	12.67

[a](Harner and Bidleman, 1998); [b](Odabasi *et al.*, 2006)

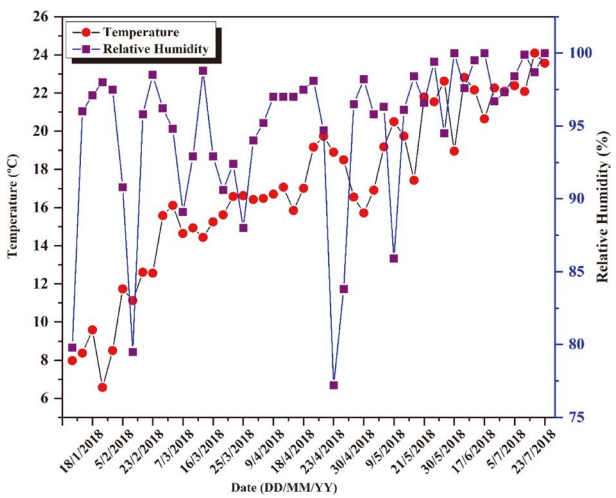

Fig. S1. Temperature (°C) and relative humidity (%) in Dhulikhel during the sampling period.

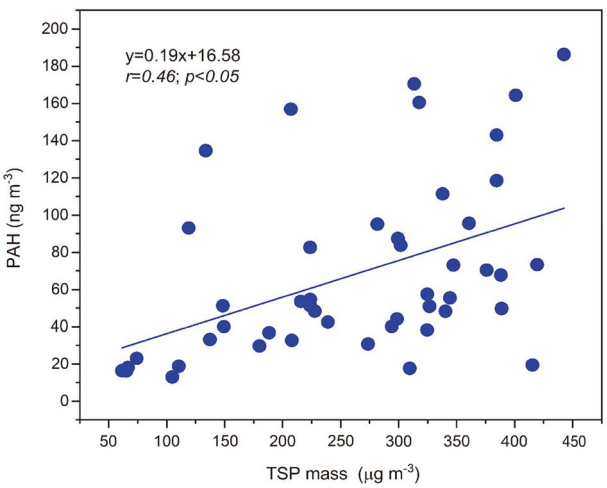

Fig. S2. Correlation between concentrations of PAHs and TSP mass in the study site.

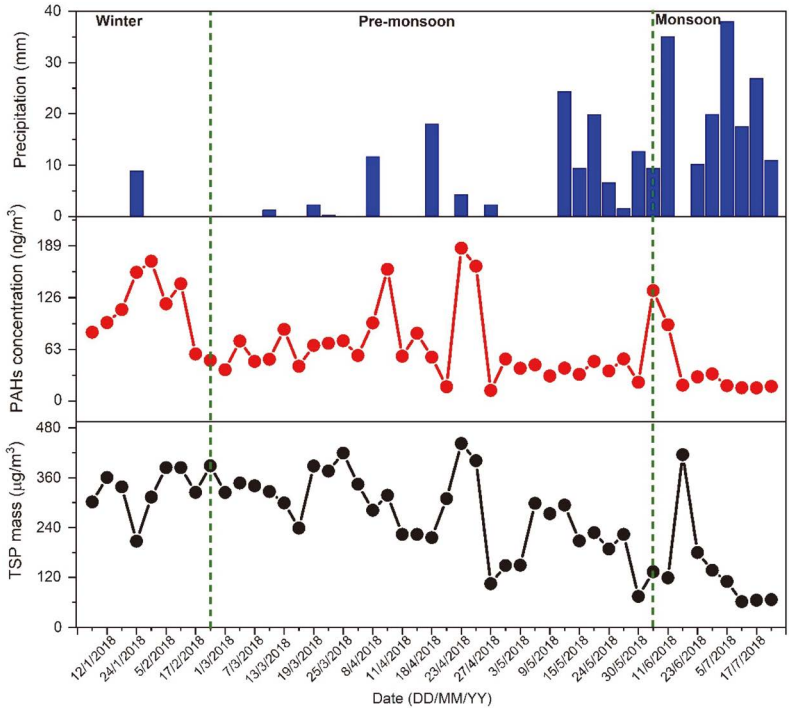

Fig. S3. Seasonal variations of TSP mass (µg/m^3) and PAH (ng/m^3) concentrations with precipitation in the study site during the sampling period.

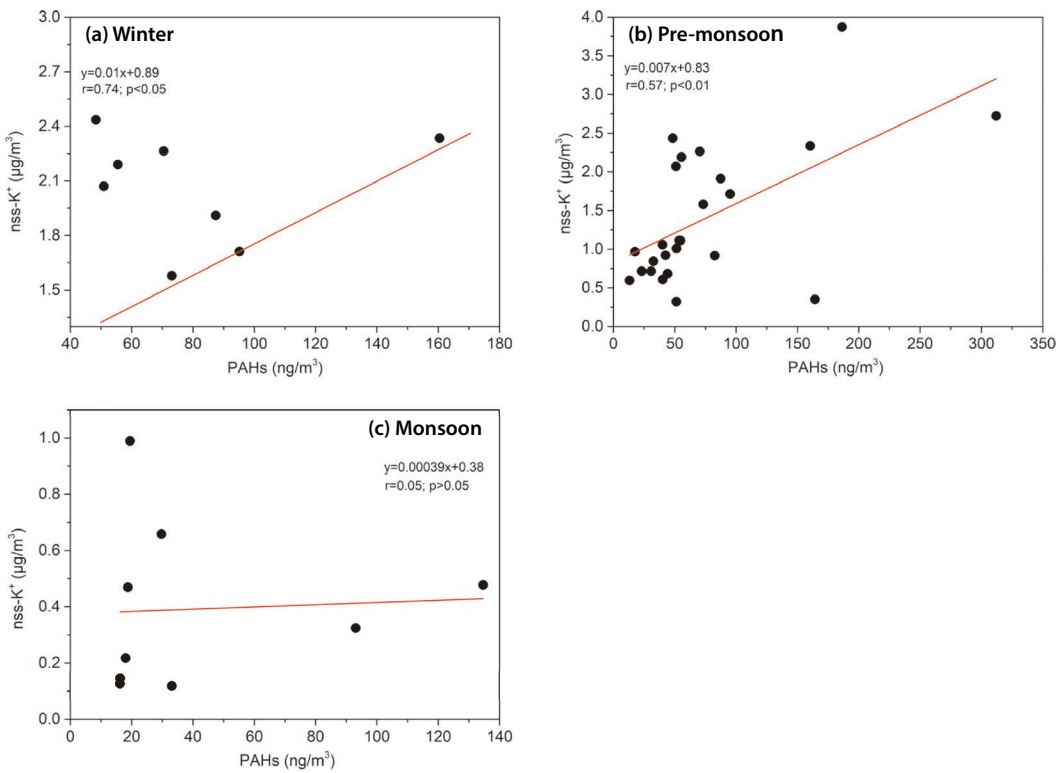

Fig. S4. Correlations coefficient between concentrations of Σ PAHs and nss-K$^+$ during (a) Winter, (b) Pre-monsoon and (c) Monsoon season.

Text S1. Details on Methods (Extraction and Analysis of PAHs) and Quality Control/ Quality Assurance

Analyses of PAHs were done at the State Key Laboratory of Cryospheric Sciences, Northwest Institute of Eco-Environment and Resources, Lanzhou, China by using Gas chromatography–Mass spectrometry (GC-MS). An ITQ 1100 GC-MS system (Thermo Electron Corporation, USA) was used equipped with a (30 m × 0.25 mm × 0.25 μm) TG-5MS capillary column. The carrier gas (high-purity helium) was used at a constant flow rate of 1.0 mL/min. The mass spectrometer was functioned at a full scan in 70 eV electron impact mode at a mass scanning range of m/z = 50–650. The temperature of the injector and the transfer line was 280°C and, the ion source temperature was 230°C. The GC oven temperature gradient was carried out: the initial temperature was 70°C, which was retained for 3 minutes. The temperature was then increased to 150°C at 25°C/min, increased to 280°C at 3°C/min and finally increased to 300°C and held for 10 minutes. Samples were examined for the fifteen PAHs listed by the USEPA as priority PAHs: including Acenaphthylene (AcPy), Acenaphthene (AcP), Fluorene (Flu), Phenanthrene (Phe), Anthracene (AnT), Fluoranthene (FluA), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chr), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno(1,2,3-cd)pyrene (IndP), Dibenzo(a,h)anthracene (DbA), and Benzo(g,h,i)perylene (BghiP). As Naphthalene (NaP) was detected with high concentrations in the laboratory and field blanks, it was not analyzed in this study.

Strict quality assurance and control procedures were followed for the analysis. The extraction and analysis of field blanks for the air samples were done using the same method as the samples. Method detection limits (MDLs) were calculated as 3 times the standard deviation of the mean blank concentrations. The detection limits were 0.15 (AcPy), 0.32 (AcP), 0.74 (Phe), 0.18 (AnT), 0.45 (Flu), 0.13 (FluA), 0.05 (Pyr), 0.04 (BaA), 0.01 (Chr), 0.07 (BbF), 0.06 (BkF), 0.03 (BaP), 0.16 (IndP), 0.06 (DbA), and 0.08 pg/m^3 (BghiP). Chrysene-d12 was added as the PAH surrogate standard to the samples before the extraction to check the extraction, cleanup, and analysis processes. The recovery efficiency of Chrysene-d12 was 69–109% for the TSP samples.

Text S2. Details on the lifetime average daily dose (LADD) estimation of PAHs

Benzo(a)pyrene (BaP) is mostly used as a marker of toxicity for all PAHs due to its high carcinogenic potency and its presence in the environment (Petry *et al.*, 1996). International Agency for Research on Cancer (IARC) has classified total carcinogenic PAH considered as probably carcinogenic to humans (BaA, BaP, and DbA) and as possibly carcinogenic to humans (BbF, BkF, and IndP) (IARC, 2010).

The equation for estimating the lifetime average daily dose (LADD) of PAHs is shown as follows:

$$\text{LADD} = \frac{\text{Cs} \times \text{IR} \times \text{ET} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times \text{cf}$$

where, LADD is the amount of intake per kilogram of body weight per day of a chemical suspected of having adverse health effects when absorbed into the body over a long period of time (mg/kg/d); Cs is the concentration of BaPeq for total carcinogenic PAH in the air (ng m^{-3}); IR is the air inhalation rate (0.83 m^3/h for adults), (0.5 m^3/h for children up to six years) and ET is the exposure time (21 h/d); EF is the exposure frequency (350 d/year); ED is the lifetime exposure duration (years), 70 years for adults and 6 years for children; BW is the body weight (kg), it was assumed that BW = 70 kg for adults and 15 kg for children; AT is the averaging time (days) for carcinogens which is ED × 365 d. So, AT for adults = 25,550 and children = 2190 days, cf is the unit conversion factor, (10^{-6}) (Bortey-Sam *et al.*, 2015; Bozek *et al.*, 2009).

REFERENCES

Bortey-Sam, N., Ikenaka, Y., Akoto, O., Nakayama, S.M.M., Yohannes, Y.B., Baidoo, E., Mizukawa, H., Ishizuka, M. (2015) Levels, potential sources and human health risk of polycyclic aromatic hydrocarbons (PAHs) in particulate matter (PM_{10}) in Kumasi, Ghana. Environmental Science and Pollution Research, 22(13), 9658–9667. https://doi.org/10.1007/s11356-014-4022-1

Bozek, F., Adamec, V., Navratil, J., Kellner, J., Bumbova, A., Dvorak, J. (2009) Health risk assessment of air contamination caused by polycyclic aromatic hydrocarbons from traffic. In: The 7th WSEAS International Conference on Environment, Ecosystems and Development (EED'09), Puerto De La Cruz, Canary Islands, Spain, December, pp. 14–16.

Harner, T., Bidleman, T.F. (1998) Octanol - air partition coefficient for describing particle/gas partitioning of aromatic compounds in urban air. Environmental Science and Tech-

nology, 32(10), 1494–1502.
IARC (International Agency for Research on Cancer)(2010) Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, 92: 1.
Odabasi, M., Cetin, E., Sofuoglu, A. (2006) Determination of octanol - air partition coefficients and supercooled liquid vapor pressures of PAHs as a function of temperature: application to gas-particle partitioning in an urban atmosphere. Atmospheric Environment, 40(34), 6615–6625.
Petry, T., Schmid, P., Schlatter, C. (1996) The use of toxic equivalency factors in assessing occupational and environmental health risk associated with exposure to airborne mixtures of polycyclic aromatic hydrocarbons (PAHs). Chemosphere, 32(4), 639–648.