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Effect through inhalation on human health of PM_1 bound polycyclic aromatic hydrocarbons collected from foggy days in northern part of India

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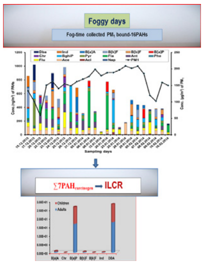
HIGHLIGHTS

- The average concentration of $PM_1 = 160.16 \pm 37.70\ \mu g/m^3$.
- Toxic equivalency factors of $\sum 7PAH_{carcinogen}$ contributes 98.51% of total PAHs.
- ILCR of B[a]P and Dibenz (a, h) anthracene was relatively much higher than other carcinogenic PAHs.
- High total ILCR for both adults and children.
- Diesel emission, combustion and long range transport are main sources for PAHs.

GRAPHICAL ABSTRACT



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ABSTRACT

We investigated the health risk from 16 polycyclic aromatic hydrocarbons (PAHs) adsorbed on submicron particles and also reported their concentrations, spatial distribution and possible sources during foggy days at Kanpur. Twenty-four urban foggy day's samples gathered from Kanpur, an urban center in North India and most densely populated city in the Indo-Gangetic plain of India, were examined for 16 PAHs (2–6 rings).The mean concentration of PM_1 was found to be $160.16 \pm 37.70\ \mu g/m^3$. $\sum 16$PAHs concentrations were 529.17 ng/m^3 with a mean of 33.07 ng/m^3. The compounds of higher molecular weight (4–6 rings) added to 70.67% of $\sum$PAHs mass concentration in the foggy day's samples. The results of source identification by using principle component analysis (PCA) and diagnostic ratios proposed that the primary sources of PAHs were vehicular emission (primarily driven by diesel fuel) and coal combustion and the secondary source. Exposure to total PAHs in the ambient air resulted in, 95% probability total ILCR (TILCR) 3.57×10^{-5} for adults and 2.08×10^{-5} for children or (~35 cancer case per million in adults and ~20 cancer case per million in children) due to inhalation in terms of ILCR were higher than the baseline value of acceptable risk (one cancer case per million people) suggesting moderate health risk to resident human population.

1. Introduction

It has been shown that urban air pollution causes ~360 000 premature deaths each year in Asia [69] although an estimated 10 500 premature deaths take place per year in Delhi, the capital of India [30]. Over the past decade, a large number of epidemiological analyses have established a definite connection between airborne particles and human mortality and/or morbidness [56]. Some studies have expressed that chemical composition of particulates, particularly the presence of small amounts of toxic

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chemicals, is a more appropriate parameter for the assessment of particulate health effects rather than their mass concentrations [22].

Human health and air quality are also adversely affected by organic aerosol. However, various kind of uncertainties exist in determining the true nature and in the quantification of effect of organic aerosols on both health and climate, ascribed to the presence of a fairly wide and complex set of organic aerosol species in the ambient atmosphere [94,95]. PAHs once adsorbed on fine particulate matter is omnipresent environmental contaminants that once released may remain in the environment for a long time and have long-range transportation [70].

In household, normally applied biomass fuels are cow dung cake, crop residues, wood, coal, remaining dried plant parts and kerosene oil, etc. [31,17,85,21,19]. The outdoor pollution in the urban areas is dominated by vehicular emission and comprises of various prooxidants [53].

Risk assessment of PAHs can be also carried out by assuming that the toxicity of all the PAHs is equivalent to that of BaP. When BaP is emitted into the atmosphere, it is distributed between the gaseous and the particulate phase, the latter being dominant due to the low BaP volatility (vapor pressure = 10^{-9} Torr) [87]. Since atmospheric particles, and especially those with smaller diameter, can be easily inhaled and absorbed in the human respiratory tract [4,47]. A chemical group of hydrogen and carbon comprising organics constitute PAHs [57,54] which get resettled in the indoor and outdoor surrounding [14,88].

Highly lipophilic, semivolatile and photosensitive PAHs are resistant to heat and corrosion [14,40]. PAHs are predominately attached with dust particles in air or sediments and adsorbed in the soil due to this they are mostly nondegradable and hydrophobic [14]. PAHs have various widespread sources including anthropogenic (industrial, domestic) and natural sources and they survive both in particle and gas phases [83,40]. Adsorption of PAHs on the surface of inorganic substances or on the outer surface of particles make them highly reactive. Molecular sign of PAHs can be useful in source identification and characteristic behavior; however, ageing can alter the characteristic behavior of PAHs [9]. Pattern on long-range trans boundary air pollution for persistent organic pollutants also includes PAHs. (United Nations Economic Commission, http://www.unece.org/env/lrtap/pops.h1.htm) [88].

The transport across biological membrane and their perniciousness is expected to be tissue-specific due to lipophilic nature of PAHs. [24]. Incomplete combustion product of petroleum products and organic materials are responsible for the large amount of released PAHs [44,66]; however, the principle cause of huge emission of PAHs is the cracking of crude petroleum, domestic waste incineration, industrial waste incineration and burning of fossil fuel [67,66].

The main objectives of the present study are to understand the distributions, identify the major sources contributing of PAHs in Kanpur ambient aerosol and to assess the leading health risks, if any, with exposure to adult and children as life time average daily dose (LADD) and their response as per incremental lifetime cancer risk (ILCR) of fog time collected submicron particulate matter.

2. Materials and methods

2.1. Study area and sampling site

Kanpur is placed 82 km north of the state capital of Lucknow and is 437 km east of Delhi. It has an area of over 605 km2 with an approximate population of 4.2 million inhabitants in its area. Kanpur is positioned on the bank of the Ganges River, center of Indo-Gangetic Plain of India and has been an important place in the history of modern India. It was recognized as Manchester of the East and one of the primary centers of industrial revolution in India. Sampling was accomplished on the roof of an 8 m high building of Centre for Environmental Science and Engineering, (CESE) within the IIT Kanpur campus. IIT Kanpur (longitude 88° 22′ E and latitude 26° 26′ N) is an educational institute outspread approximately 4.3 km2 and accepting a residential population of more than 8000. Industrial or commercial activity was not prevalent inside the institute. The campus is placed about 15 km north of the city in the upwind direction. Vehicular population mainly consists of two wheelers and cars were observed within the campus. In addition, there is a dense vehicular traffic on a national highway situated about 1.5 km east of the sampling site [65].

2.2. PM_1 sampler, sampling schedule and collection of quartz fiber filters

Our previously built PM1 sampler was used for sampling [27,29], for details about validation of sampler refer to [16,28]. 8 h per day was sampling time during a total of 24 days of fog period (15 December 2013–16 February 2014). 47 mm diameter of Whatman QM-A quartz fibre filter was employed for collection of submicron particles. Blank was maintained 10% of the total numbers of gathered filters in each month and similar gravimetric and chemical analyses were carried out on those as the sampled filters. For details see the [65]. We identified the specific foggy days using information available at IITK Mplnet [64] http://mplnet.gsfc.nasa.gov/data.html.

2.3. Procedure of PAHs analysis

Small pieces of seventy five percent areas of 47 mm of each quartz fibre filter were used for PAHs analysis. Toluene was applied as extraction solvent for both samples and blanks by using ultrasonicator. According to [96] toluene was better compared to other solvents such as dichloromethane, benzene/methanol etc. due to its high recovery mainly for higher boiling PAHs. Prepared toluene extracts were decanted into centrifuge tubes, and the filter papers were further extracted with 10 ml of toluene, and then, the solution was ultrasonicated for 20 min. Eventually, leftover filter papers were extracted with 5 ml of toluene and ultrasonicated for 5 min. Toluene extracts were shifted into the centrifuge tubes and 0.2 ml of acetonitrile was added to each tube and samples were filtered through 0.22 μm membrane filters (Millipore). Samples were then evaporated to near dryness by using rotavapor. An additional 2 ml of acetonitrile was added and samples were re-evaporated to near dryness. The final volume of each sample was set to 1 ml with acetonitrile, and samples were again filtered through 0.22 μm filters into vials. The PAH examined by HPLC/PDA detector were: naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Acl), phenanthrene (Phe), anthracene (Ant), fluorene (Flu), fluoranthene (Fla), benz[a]anthracene (B[a]A), pyrene (Pyr), chrysene (Chr), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), dibenz [a,h]anthracene (Dba), benzo[g,h,i] perylene (BghiP), indeno [1,2,3-c,d]pyrene (Ind). It was found that fourteen out of the sixteen PAH defined by USEPA as priority pollutants were present in significant amounts in the collected samples [97]. The elucidated extracts were stored in a refrigerator until further analysis. For every PAH in the concentration ranges up to a maximum of 1000 ng/ml linear calibration graphs were found [65].

2.4. Quality control and quality assurance

HPLC was equipped with photo diode detector at a specific wavelength of 254 nm (model: Waters 2998) and the flow rate