



# Annual trends in occurrence of submicron particles in ambient air and health risk posed by particle bound metals



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## HIGHLIGHTS

- PM<sub>1</sub> and metals concentration in ambient air were measured.
- Contamination level of metals assessed by Geo-accumulation Index.
- Health risk of metals assessed by Hazard Index for children and adults.
- Non-carcinogenic risk existed for children.
- Cancer risks found were above the safe limit.

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## ABSTRACT

Risk analysis is highly important in toxicology and public health studies. Health risk related to exposure to toxic metals of PM<sub>1</sub> was assessed. Concentrations of 13 heavy metals, adsorbed to submicron particulate matter PM<sub>1</sub> were experimentally examined but only 12 metals were found at detectable levels inside IIT Kanpur campus in 2008–2009 for all months excluding June and October. A total of 90 samples collected for 8 h sampling time by a single stage round nozzle, grease impaction substrate based impactor type PM<sub>1</sub> sampler were analysed by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry). Results showed daily average PM<sub>1</sub> concentration is  $102.46 \pm 35.9 \mu\text{g}/\text{m}^3$  and metal concentration followed the trend: Ca > Fe > Mg > Zn > Pb > Cu > Cr > Ni > Se > Cd > V > As. Contamination level assessment using geo-accumulation index showed Ca, Fe and Mg exhibited non contamination whereas metals like Cr, Zn, As, Cd, Pb, Se, Ni and Cu exhibited ranges from moderate to extreme contamination. Ingestion is found to be the major exposure pathway for heavy metals. Non-carcinogenic health risk assessment for Pb, Cd and Cr (HI > 1) signified strong chances of adverse impact on children whereas adults are well under safe limit. Cancer Risk for adults and children followed the same decreasing order, Cr(VI) > Cd > Ni > As > Pb. It was found to be higher than permissible limits ( $10^{-6}$ ) for adults and children both.

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## 1. Introduction

International Agency for Research on Cancer (IARC), specialized cancer agency of the World Health Organization, in October 2013 classified outdoor air pollution as Group 1 carcinogenic to humans (IARC, 2013). An earlier study by the agency in 2010 on link between air pollution and cancer (Straif et al., 2013) reported that 223,000 deaths from lung cancer worldwide resulted from air pollution. In India there has been lots of research done across the

country regarding particulate matter PM<sub>2.5</sub> ( $d \leq 2.5 \mu\text{m}$ ) and PM<sub>10</sub> ( $d \leq 10 \mu\text{m}$ ) (Khillare and Sarkar, 2012; Pandey et al., 2013; Das et al., 2015) and pollutant concentrations were found to be well above the permissible national standards. Information on pollutant load on PM<sub>1</sub> is sparse. PM<sub>1</sub> may comprise of the primary particulate matter and heavy metals, emitted directly into the atmosphere from sources such as road traffic, resuspension of road dust, construction and agricultural activities, power plants, industrial processes, biomass burning, etc., as well as secondary pollutants formed through the photochemical transformations of gas phase species (Hildemann et al., 1991; Schauer et al., 1996). Particulate matter from these sources may contain hazardous metals and can have both carcinogenic and non-carcinogenic effects. Due to heavy

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metals with well-known toxicity and low biodegradation, as well as their menace to the environment and public health, they have been of scientific interest for many years and have been widely studied in various environmental and biological compartments (Hall, 2002; Ferreira-Baptista and De Miguel, 2005).

Several epidemiological studies (Schwartz et al., 1996; Pope, 2000) have suggested a statistical association between health effects and ambient fine particle concentrations, especially the sub-micron particulate matter PM<sub>1</sub> ( $d \leq 1 \mu\text{m}$ ) that can penetrate deep into the alveolar region of the lungs easily, stay there for a long time and then enter the blood circulation system. It has been found that the particle size had a significant influence on assessment of human risk (Cao et al., 2012). Many studies have shown that the smaller the size and solubility of the particles, the increased surface to volume ratio for finer particles causes higher toxicity through mechanisms of oxidative stress and inflammation (Valavanidis et al., 2008). It has been reported that most of the toxic metals accumulate in the smaller particles (PM<sub>2.5</sub> or less) (Ravindra et al., 2008). Recent studies have linked PM to acute pulmonary problems (such as bronchitis and asthma) and to cardiovascular problems (such as congestive heart failure and ischemic heart disease), altered host defence mechanisms, cancer, chronic respiratory problems, low birth weight and infant mortality (Wang et al., 1997; Woodruff et al., 1997). Transition metals, such as iron, vanadium, nickel, chromium, copper, and zinc, have been particularly cited a most likely to be toxic on the basis of their ability to support electron exchange (Ghio et al., 1996) and catalyse and generate ROS (Reactive oxygen species) in biological tissues (Chen and Lippmann, 2009). ROS, such as hydroxyl radicals (OH·), are thought to be involved in various forms of lung injury and are considered to be both genotoxic and carcinogenic (Knaapen et al., 2004).

As a result, quantitative analysis of human health risks has become increasingly and significantly important, both for estimating the degree of risk associated with chemical pollutants and for selecting preventive strategies that can mitigate these risks to an acceptable level. The United States Environment Protection Agency (US EPA) recommended in a recent report on air quality criteria for particulate matter that PM<sub>1</sub> could be used as the standard cut-off point for fine particles, as human respiratory symptoms are highly linked with PM<sub>1</sub> levels. However, the advantage of a PM<sub>1</sub> standard compared to the current PM<sub>2.5</sub> standard is not clear (Hieu and Lee, 2010).

Investigations on health risk caused by exposure to Particulate matter in India have been very few and negligible in terms of PM<sub>1</sub>. By using the health risk assessment method provided by US EPA, this study attempts to evaluate the carcinogenic and non-carcinogenic health risk to both adults and children caused by exposure to PM<sub>1</sub>, through three different exposure pathways including inhalation, ingestion and dermal contact. Calculations are based on the concentrations of 8 heavy metals (As, Cd, Cr, Cu, Ni, Pb, V and Zn) recorded on PM<sub>1</sub> in ambient air at IIT Kanpur through air samples collected year round in 2008. The calculations represent a broad category of chronic toxicity including mutagenicity, neuro-toxicity developmental toxicity and reproductive toxicity. The study results describe the air quality of the campus of IIT Kanpur and could help the physicians, public health officials and the general public to get a better view about the health risks of heavy metals in PM<sub>1</sub> via ingestion, dermal contact and inhalation exposure.

## 2. Methodology

### 2.1. Sampling site and sources of air pollution

The city chosen for this study, Kanpur (latitude 26.5°N and

longitude 80.3°E at 142 m above mean sea level), is situated in the central part of Indo-Gangetic Plain and represents an urban setting. Sampling was conducted between July 2008 to May 2009 inside the IIT Kanpur campus on the roof of a 12 m high building (Western Lab Extension) from 9 am to 5 pm. Continuous drift of vehicles of different types on a Grand Trunk Road (national highway) crossing through the centre of city, several small scale industries including leather tannery, automobile production units, cotton mills etc., coal based power plants (Panki) and diesel generators are the major sources of air pollution. In addition, aerosols emitted locally can be carried to distant places by wind causing impact on regional scale. The campus of IIT Kanpur which is an educational institute with residential campus, lies about 15 Km north of Kanpur city. There are negligible industrial and commercial activities except some regular construction events on campus and it lies in the upwind direction from city for major part of the year. Vehicle type inside campus comprises mainly of two wheelers and cars (Jai Devi et al., 2009). Fig. 1 shows the land use pattern for the Kanpur city, including the exact location of sampling site for this study (Black Dot).

### 2.2. Sampling procedure

Air sampling was carried out using a single-stage round nozzle, a grease substrate-based impactor type PM<sub>1</sub> sampler earlier developed in the lab at IIT Kanpur (Gupta et al., 2010). Total 90 samples spread all across the year except the months of June and October, and additionally 10 field blanks were collected. All samples were collected over an 8-hr period on the sampling day (Chakraborty and Gupta, 2010).

#### 2.2.1. Instrument details

The sampler ( $d_{50} = 1.05 \mu\text{m}$  and GSD = 1.24) has been validated with polydisperse artificial aerosol generated in the lab and measured using an APS (Aerodynamic Particle Sizer, model 3021, TSI Inc., USA) following well established methods for impactor characterization (Gupta et al., 2004). Flow rate of the sampler was 10 LPM (measured by rotameter, calibrated using mass flow meter, Dakota Inc., USA) and a backup PTFE or Teflon filter with 46.2 mm collection diameter was used for PM<sub>1</sub> collection. The overall pressure drop through the sampler, including a Teflon backup filter, was 18.5 cm of water. Teflon filters were used for following reasons: (a) they are chemically very inert and consist of very little impurities which laid down them especially worthy for trace element analysis; (b) very little moisture absorption capacity and high PM collection efficiency; (c) can withstand on a very wide range of weather conditions without any deformation.

### 2.3. Gravimetric and chemical analysis

All the filter papers used for the sampling were pre-conditioned and post-conditioned in a controlled environment at 25 °C and 40% RH for 24 h before and after the sampling (Lin and Lee, 2004). All pre-conditioned and post-conditioned filters were then weighed three times using a microbalance (Mettler Toledo). An additional 10% of the total number of exposed filters in each season was kept as blank and subjected to exactly similar analytical procedure as the exposed filters and then both the gravimetric mass and chemical composition data found were corrected subsequently using the blank values. The difference in weight of filters before and after sampling gave the collected Particulate matter (PM<sub>1</sub>) mass and hence concentration after dividing PM<sub>1</sub> mass by the sampled volume of air (in this study it was a constant = 4.8 m<sup>3</sup>). The additional details regarding the handling and usage of filter papers and subsequent solution preparation for elemental analysis are provided elsewhere (Chakraborty and Gupta, 2010).

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