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

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HIGHLIGHTS

- PM_1 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_1 was assessed. Concentrations of 13 heavy metals, adsorbed to submicron particulate matter PM_1 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_1 sampler were analysed by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry). Results showed daily average PM_1 concentration is 102.46 ± 35.9 μg/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.

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 $PM_{2.5}$ ($d \leq 2.5$ μm) and PM_{10} ($d \leq 10$ μm) (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_1 is sparse. PM_1 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 submicron particulate matter PM_1 ($d \leq 1$ μm) 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 ($PM_{2.5}$ 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 ($OH\cdot$), 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_1 could be used as the standard cut-off point for fine particles, as human respiratory symptoms are highly linked with PM_1 levels. However, the advantage of a PM_1 standard compared to the current $PM_{2.5}$ 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_1. 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_1, 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_1 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, neurotoxicity 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_1 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_1 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 ($d_{50} = 1.05$ μm 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_1 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_1) mass and hence concentration after dividing PM_1 mass by the sampled volume of air (in this study it was a constant = 4.8 m^3). 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).

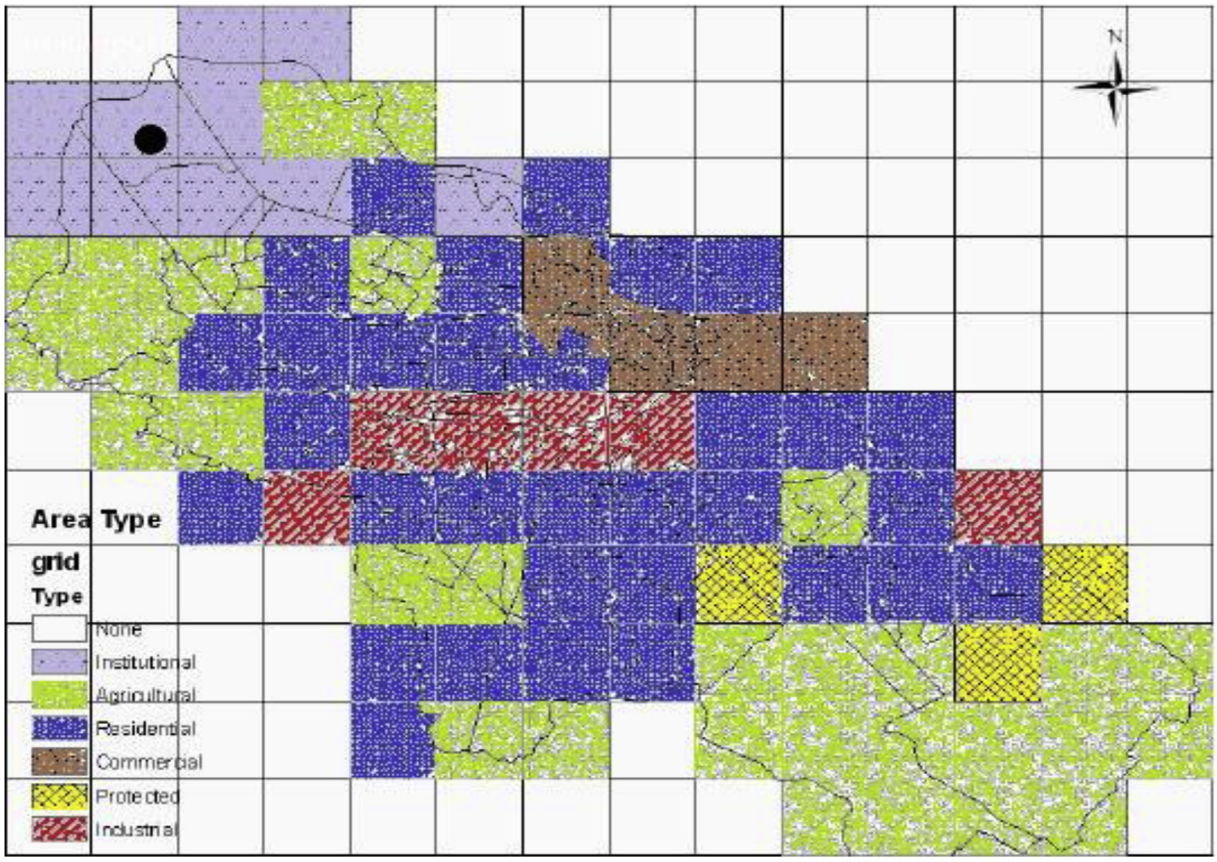

Fig. 1. Map of Kanpur city depicting the land use pattern and the sampling site, IIT Kanpur (adapted from Chakraborty and Gupta, 2010).

The elemental analysis was performed using ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry, ICAP 6300 Thermo Inc.). This instrument employs superheated Argon plasma produced at 7000–10,000 K to breakdown and excite the atoms of the different elements and this allows identification of elements from the characteristic wavelength emitted during the excitation process, it's a fairly rapid process and can identify up to 60 elements simultaneously. 13 elements were selected for our analysis: As, Ca, Co, Cr, Cd, Mg, Fe, Ni, Pb, Cu, Zn, V, Se. Out of these, 12 were found be present at detectable levels in the samples and Co was found to be mostly below the detection limit of the instrument.

2.4. Contaminant level assessment

Caeiro et al., 2005, Kong et al., 2012 and Li et al., 2013 analysed pollution indices to assess heavy metals concentration and classified them mostly in two indices, Geo-accumulation Index (Igeo) and Enrichment Factor (EF). In this paper Geo-accumulation Index is discussed in detail.

2.4.1. Geo-accumulation index

The geo-accumulation index (Igeo) assessment method is defined in order to determine metal contamination including sediments, particles etc. by comparing present concentration with of earth crust concentration. Results could be useful for regulators and engineers as an indicator for the current contamination level. The geo-accumulation index was calculated by the following equation.

$$Igeo = \log_2 \frac{Cx(sample)}{1.5 * Cx(crust)} \quad (1)$$

Where, $Cx(sample)$ represents the measured concentration of metal 'x' and $Cx(crust)$ is the geochemical background value (earth crust) of metal 'x' (Lide, 2008). The constant 1.5 allowed to examine natural fluctuations in the content of a given substance in the environment and to detect very minute anthropogenic influences. The Geo-accumulation Index consists of 7 classes (Table 1). The metal concentrations in class 6 may be hundred times greater than background value (Yaqin et al., 2008). Igeo values > 1 may indicate influence of anthropologic sources.

2.5. Human exposure and health risk assessment model

Both cancer and non-cancer risk due to exposure to particle bound metals in ambient air have been calculated. Methods used for determination of exposure dose in three major exposure

Table 1
Seven classes of Geo-accumulation Index.

Class	Igeo value	Contamination level
0	Igeo $\leq$ 0	Uncontaminated
1	0 < Igeo $\leq$ 1	Uncontaminated to moderately contaminated
2	1 < Igeo $\leq$ 2	Moderately contaminated
3	2 < Igeo $\leq$ 3	Moderately to heavily contaminated
4	3 < Igeo $\leq$ 4	Heavily contaminated
5	4 < Igeo $\leq$ 5	Heavily to extremely contaminated
6	Igeo $\geq$ 5	Extremely contaminated

pathways, followed by risk assessment techniques are described in this section.

2.5.1. Exposure dose

The model used in this study to compute the exposure of humans to heavy metals in ambient particulate matter is based on those developed by US Environmental Protection Agency (EPA) human health evaluation method. Potential exposure can occur through three different pathways including ingestion, inhalation and dermal contact (Ferriera-Baptista and De Miguel, 2005; Hu et al., 2012; Kong et al., 2012). Exposure is defined in terms of daily dose and computed individually for each metal and each exposure pathways. Equations defining the Exposure dose through each pathways are given below.

Average daily exposure dose of heavy metals through ingestion (ADD_{ing}, mg/kg/day)

$$ADD_{ing} = \frac{C*IngR*EF*ED*CF}{BW*AT} \quad (2)$$

Average daily exposure dose of heavy metals through inhalation (ADD_{inh}, mg/kg/day)

$$ADD_{inh} = \frac{C*InhR*EF*ED}{BW*AT*PEF} \quad (3)$$

Average daily exposure dose of heavy metals through dermal contact (ADD_{derm}, mg/kg/day)

$$ADD_{derm} = \frac{C*SA*AF*EV*ABS*EF*ED*CF}{BW*AT} \quad (4)$$

where, C is the concentration of metals in PM_1 (mg kg^{-1}); IngR is the ingestion rate (mg day^{-1}) which in this study was 30 (adults) and 60 (children); InhR is the Inhalation rate (m^3 day^{-1}) which in this study was 7.63 (adults) and 20 (children); EF is the Exposure frequency which in this study was 180 days/year; ED is the Exposure duration which in this study was 24 year (adults) and 6 year (children); BW is the Body weight which in this study was 70 Kg (adults), 15 Kg (children); SA is the Skin surface area parameter which in this study was 5700 cm^2 (adults), 2800 cm^2 (children); AF is the Adherence factor of soil to skin which in this study was 0.07 mg/cm^2/event (adults), 0.2 mg/cm^2/event (children); EV is the Events frequency which was 1events/day; ABS is the Dermal absorption fraction which in this study was 0.001; PEF is the Particle emission factor 1.36 * 10^9 m^3/kg; AT is the Averaging time for Non-carcinogens which in this study was ED * 365 days/year; CF is the Conversion factor which was about 10^{-6} kg/mg. All the parameters used in calculation can be found from the reports published by US EPA (US EPA, 2004a, b; US EPA, 2007; US EPA, 2009).

2.5.2. Non carcinogenic health risk

Hazard Quotient (HQ) and Hazard Index (HI) are used to measure the non-carcinogenic health risk of heavy metals in ambient particles. As the average daily dose for three pathways have been computed, HQ can be calculated by dividing the Average Daily Dose to a specific reference dose (RfD).

$$HQ = \frac{ADD}{RfD} \quad (5)$$

The reference dose is an approximation of maximum allowable risk on human population through daily exposure taken into account of sensitive group during a lifetime. If HQ < 1 (average daily dose is less than reference dose), it implies no adverse impact on health. Otherwise, if HQ > 1 (average daily dose is greater than reference dose), then there are chances that the exposure pathway may adversely affect human health (Zheng et al., 2010).

For non-carcinogens there exists the assumption of threshold, below which there is no toxic response. The reference dose values used here have been taken from various studies (Kong et al., 2012; Li et al., 2013; Du et al., 2013) and are summarised in Table 2.

Hazard Index (HI) for a pollutant is the sum of all the Hazard Quotient for multiple exposure pathways (Ferriera-Baptista and De Miguel, 2005; Zheng et al., 2010). HQs computed for individual metals for each pathway are added to compute HI to estimate the risk of all metal contaminants.

$$HI = \sum_{i=1}^{i=2} HQi \quad (6)$$

If HI < 1, there is no significant risk of non-carcinogenic effects whereas if HI > 1, there is likelihood that non-carcinogenic effects may occur, likelihood of which tends to increase as the HI increases (Zheng et al., 2010).

2.5.3. Excess cancer risk

Excess cancer risks (ECRs) have been estimated as the incremental probability of a person developing cancer over a lifetime as a consequence of total exposure to the potential carcinogen. ECR is calculated by using the given formula (US EPA, 2011; Hu et al., 2012).

$$ECR = \frac{C*ET*EF*ED*IUR}{AT} \quad (7)$$

Where, C is the concentration of pollutant (μg/m^3), IUR is the inhalation unit risk (μg/m^3)$^{-1}$, AT is the average time for carcinogens (70 year × 365 days/year × 24 h/day), ET is the Exposure time which in this study was 8 h/day and other parameters are earlier mentioned. Carcinogens are considered non-threshold, meaning exposure of any amount of carcinogens will cause likelihood of cancer and the safe amount of carcinogens is "zero". The data on the carcinogenic types and the inhalation unit risk of the metals is obtained from the USEPA database for IRIS (integrated information risk system). The reference values of carcinogenic risk through dermal exposure and ingestion were not provided by the USEPA, so in our study we have considered only carcinogenic risk of metals through inhalation pathway. If the value of risk falls between the ranges (10^{-6}-10^{-4}) then the contamination likely does not produce carcinogenic risk (Hu et al., 2012).

3. Results and discussions

3.1. PM_1 and particle bound metals concentration

The PM_1 and particle bound metals concentration in the terrace of WLE building at IIT Kanpur obtained from the experimental study have been reported by Chakraborty and Gupta, 2010, and will only be summarised here.

The daily mean concentration of PM_1 and its particle bound elements for this study are reported on seasonal basis in the original study, but here in this study average daily concentration is considered. The daily mean concentration of PM_1 is about 102.46 ± 35.9 μg/m^3 with lowest average concentration (30.1 μg/m^3) observed during monsoon season and highest average concentration (199 μg/m^3) observed during winter season. Metals mass contributed about average 5 percent of total PM_1 mass. Similar to PM_1, the elemental mass concentrations varied significantly in different seasons. Among the 13 elements analysed Co (Cobalt) was found to be below detection limit all through sampling and As (Arsenic) was only detected for winter months January and

Table 2
Recommended values of Reference Doses (RfD) (mg kg^{-1} day^{-1}).

Heavy metal	As	Cd	Cr	Cu	Ni	Pb	V	Zn
RFD_{ing}	3.00E − 04	1.00E − 03	3.00E − 03	4.00E − 02	2.00E − 02	3.50E − 03	7.00E − 03	3.00E − 01
RFD_{inh}	3.00E − 04	1.00E − 03	2.86E − 05	4.02E − 02	3.52E − 03	3.52E − 03	7.00E − 03	3.01E − 01
RFD_{der}	1.23E − 04	1.00E − 05	6.00E − 05	1.20E − 02	5.40E − 03	5.25E − 04	7.00E − 05	6.00E − 02

RFD_{ing}: Ingestion reference dose.
RFD_{inh}: Inhalation reference dose.
RFD_{der}: Dermal contact reference dose.

December. Among the elements analysed, the daily mean concentration followed the order: Ca > Fe > Mg > Zn > Pb > Cu > Cr > Ni > Se > Cd > V > As (Table 3). Metals of crustal origin, Ca, Fe and Mg, were found to be in higher order compared to other elements and as expected, showed high correlation with each other. Metals like As, Cd, Cr, Cu, Zn, Ni, Se were found to be higher during winter seasons which was in concordance with other studies (Wang et al., 2006).

Table 3 present comparison of concentration of PM_1 and its particle bound metals at different geographical locations reported and those measured in this study at IIT Kanpur. There have been studies regarding PM_1 but metals concentration have not been reported (Liu et al., 2015; Pérez et al., 2008a; Mbengue et al., 2014) so the number of studies reported here are limited. It can be observed that among all the studies mentioned, the PM_1 and metals concentration are higher at IIT Kanpur (Our study). PM_1 concentration ranges from 3 to 38 times higher than studies listed. Similarly the metals concentration were mostly one order higher than other studies. Concentrations of Ca and Fe are higher compared to other elements for all studies listed except Istanbul where Zn dominates Fe as the sample were collected at road intersections (Onat et al., 2013), which can be because crustal sources are contributing commonly in large amount. The concentration of all elements in this study are 3–100 times higher than a similar study done for PM_1 during spring time at residential area of Ulsan city in South Korea (Hieu and Lee, 2010). A similar study on an academic campus in Hunan University, China (Liu et al., 2015) reported $PM_{1.1}$ concentration around 57.67 μg/m^3 which is almost half times the levels reported in our study. This overall comparison signifies PM_1 and trace metals concentration in ambient air at IIT Kanpur premises is poor compared to international studies which ultimately refers to uncontrolled industrial, vehicular and other anthropogenic activities.

3.2. Geo-accumulation index (Igeo)

The Geo-accumulation Index for heavy metals in particles collected in PM_1 are presented in Fig. 2. Based on Seven classes of Geo-accumulation Index listed in Table 1, Ca, Fe and Mg are uncontaminated (Igeo ≤ 0), V lied in the range of uncontaminated to moderately contaminated (0 < Igeo ≤ 1), Cr lied in between moderate to heavily contamination (2 < Igeo ≤ 3), Ni and As signified heavily contamination (3 < Igeo ≤ 4), Cu and Zn signified heavy to extreme contamination (4 < Igeo ≤ 5) and Cd, Pb and Se signified extremely contamination (Igeo ≥ 5). Also heavy metals including V, Cr, Ni, As, Cu, Zn, Cd, Pb and Se indicated contribution from anthropologic sources (Igeo>1). The Enrichment factor have also been calculated for the daily mean metal concentration and is mentioned in Supplementary Information. Enrichment Factor and Geo-accumulation index showed strong correlation with each other: Igeo increases with increasing EF (Supplementary information). Interestingly, it can be noted that Igeo increase with the

Table 3
Concentration of PM_1 and their metals concentrations at different locations (μg/m^3).

Site	PM1(N)	As	Ca	Cd	Cr	Cu	Fe	Mg	Ni	Pb	Se	V	Zn
[a]IIT Kanpur[1], India	1.0E + 02 (90)	2.4E − 03	1.7E + 00	3.4E − 02	1.1E − 01	2.1E − 01	1.1E + 00	7.2E − 01	9.2E − 02	2.3E-01	7.4E − 02	1.6E − 02	4.5E − 01
Barcelona[2], Spain	1.9E + 01 (108)	6.0E − 04	–	3.0E − 04	1.2E − 03	1.2E − 02	–	–	3.0E − 03	1.7E − 02	3.0E − 04	6.0E − 03	4.8E − 02
Tito Scalo[3], Italy	8.0E + 00 (327)	–	9.9E − 01	4.0E − 03	3.8E − 02	4.0E − 03	1.1E − 01	2.9E − 02	6.0E − 03	1.2E − 02	–	–	6.0E − 03
Mount Cimone[4], Italy	7.1E + 00 (24)	–	9.0E − 03	–	–	–	8.5E − 03	–	–	2.1E − 03	–	–	5.9E − 03
Istanbul[5], Turkey	2.2E + 01 (17)	6.9E − 04	2.9E − 01	–	5.8E − 03	3.6E − 03	2.7E − 02	3.1E − 02	–	–	–	2.2E − 04	1.0E − 01
Whyalla[6], Australia	2.7E + 00 (10)	–	–	–	1.5E − 03	1.0E − 03	9.9E − 02	–	1.8E − 03	–	–	1.1E − 03	4.1E − 03
[b]New South Wales[7], Australia	6.0E + 00 (10)	–	–	–	1.5E − 03	8.7E − 03	4.3E − 01	–	3.1E − 03	–	–	9.6E − 04	5.3E − 02
[c]Ulsan[8], South Korea	2.2E + 01 (NM)	–	4.5E − 01	3.0E − 03	6.0E − 03	2.1E − 02	2.0E − 01	2.6E − 01	1.5E − 02	4.3E − 02	–	–	1.3E − 01

[1]Chakraborty and Gupta, 2010.
[2]Pérez et al., 2008b.
[3]Caggiano et al., 2010.
[4]Marenco et al., 2006.
[5]Onat et al., 2013.
[6,7]Mohiuddin et al., 2014.
[8]Hieu and Lee, 2010.
N = Number of samples; NM = Not mentioned.
[a] PM_1 is reported for IIT Kanpur (Our study) by taking average of all seasons.
[b] PM_1 is reported for New South Wales by taking average of sites RT, CR and MQ.
[c] PM_1 is reported for spring season in Ulsan city.

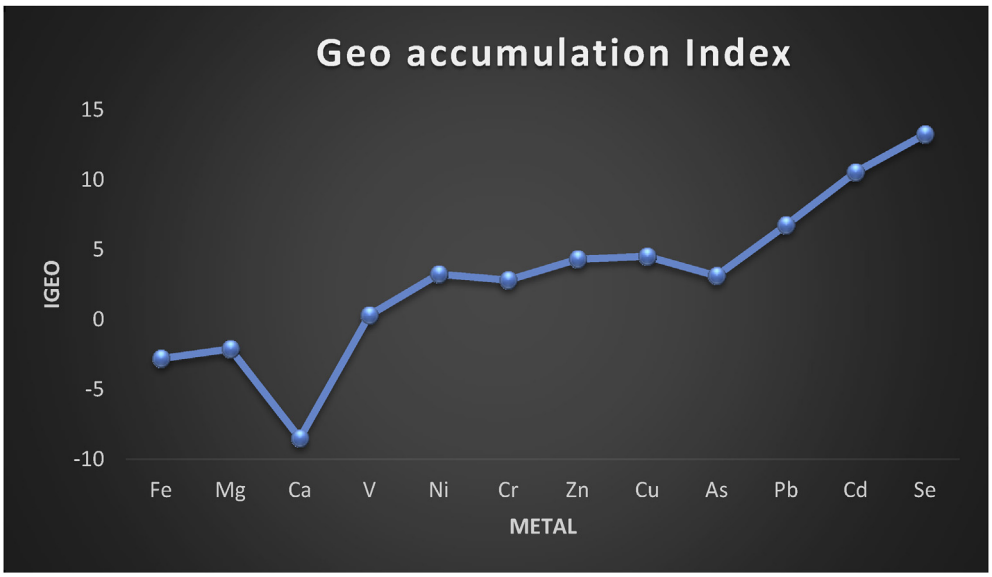

Fig. 2. Geo-accumulation Index for metals in PM_1.

increase of atomic number of elements.

3.3. Metal exposure dose

Variation of average daily dose (ADD) for all metals in PM_1 for the mentioned three different exposure pathways including inhalation, ingestion and dermal exposure are evaluated. The results are presented in Fig. 3. Results for both adults and children are included in the same figure to permit comparison. The average daily dose through different exposure pathways for both adults and children follow the same trend, $ADD_{ing} > ADD_{der} > ADD_{inh}$. The ingestion exposure pathway is found to be 2 to 4 orders higher than other pathways. There was similar study reported by Kong et al., 2011 which showed the similar trend among the adult and children for the exposure pathways trend. Among all the metals Ca and As are found to have maximum and minimum average daily dose for all the respective pathways. It is alarming to note that the for all the pathways the average daily dose for children is ten times higher than dose for adults which means on the whole children are exposed to more metals than adults (Kong et al., 2011; Liu et al., 2015; Xu et al., 2015). This data presents results based only on risk caused by exposure to metals. Determination of exposure dose for other toxic compounds like Polycyclic Aromatic Hydrocarbons are needed to compare risk posed and perform overall risk assessment.

3.4. Assessment of non carcinogenic health risk

The results for HQ and HI are presented in Fig. 4. The HQ and HI values for metal Fe, Mg, Ca and Se could not been computed as the RfD values for different exposure pathways are not established by USEPA and also not reported by other research studies probably because these are essential metals for the growth of humans and references doses may be in higher order as compare to metals concentration reported. Adults and Children follow similar decreasing trend for Hazard Quotient for all metals,

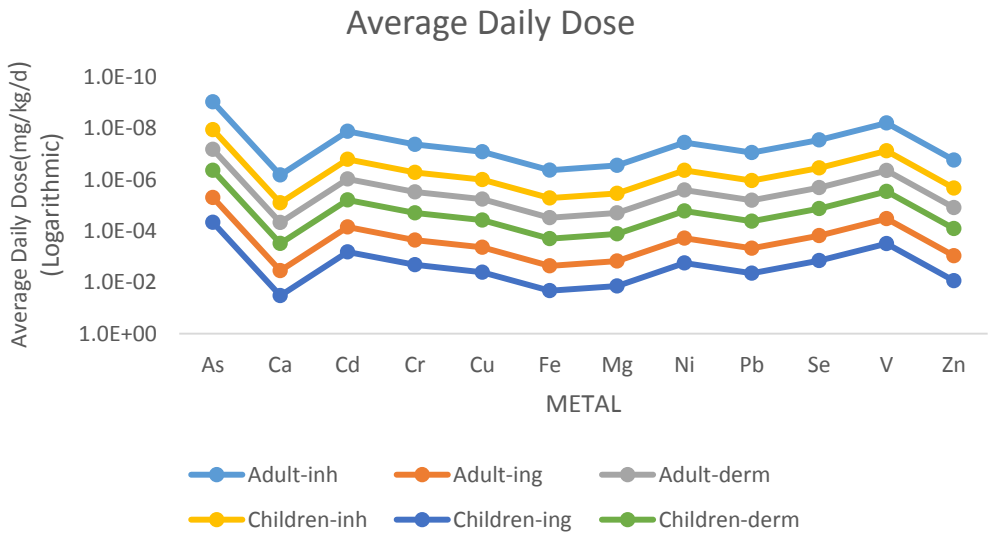

Fig. 3. Average daily dose of metals (mg/kg/day) on PM_1 for different pathways for adults and children.

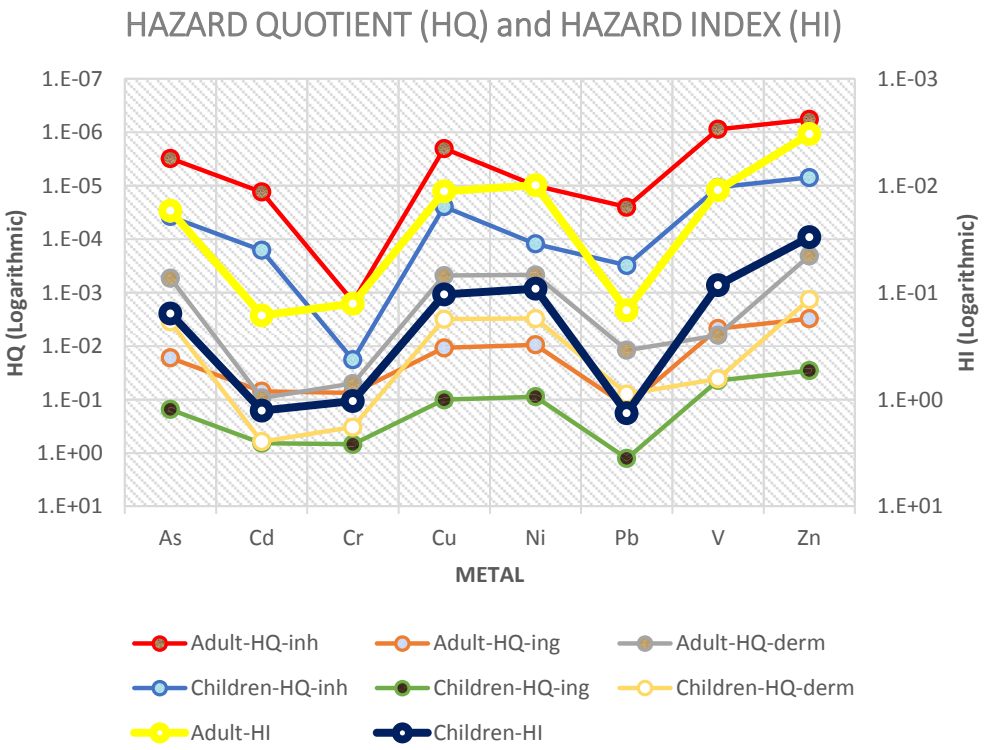

Fig. 4. Hazard Quotient HQ and Hazard Index (HI) for adults and children respective to metals exposure pathway.

HQ_{ing} > HQ_{der} > HQ_{inh} except V and Cd which followed HQ_{der} > HQ_{ing} > HQ_{inh}. The HQ value for all metals were all below 1 except Pb in case of children for which HQ_{ing} is 1.26. The average HI value of metals for adults and children followed the order: Pb > Cd > Cr > As > Cu > Ni > V > Zn. It is to be noted that the HI (children) is greater than HI (adults) by approximately 10 times. Out of 8 metals 5 were under the safe limit (HI < 1) for children except Pb (HI = 1.34), Cd (HI = 1.27) and Cr (HI = 1.04) whereas in case of adults, HI values for all metals are well under limit one. Thus Pb, Cd and Cr concentration in PM_1 show likelihood for non-carcinogenic health adverse effects on children and hence the health risk can't be overlooked in the IIT Kanpur premises for the children group. The average HI value for the adults for all the heavy metals are well under the safe limit meaning that there is no non-carcinogenic adverse impact on adults.

3.5. Excess cancer risks (ECRs)

ECRs for carcinogenic risk of metals through inhalation pathway has been computed as described earlier by using Eq. (7) and results are presented in Table 4. As shown in the table, five metals including As, Cd, Cr, Ni and Pb are among the thirteen metals analysed in this study, are either known or probable carcinogens through inhalation pathway (source: US EPA's weight-of-evidence, IRIS, 1995). There are two forms of chromium persisting in the atmosphere Cr(III) and Cr(VI). However Cr(VI) has been only reported to be carcinogenic. It is known that the concentration ratio of carcinogenic Cr(VI) to non-carcinogenic Cr(III) is about 1:6. Henceforth the concentration of carcinogenic Cr(VI) used for computing carcinogenic health risk was taken as one seventh of total concentration of chromium in ambient air (Mancuso, 1975; US EPA, 2004a, b; Massey et al., 2013). The IUR value was taken from IRIS (Integrated Risk Information System) (Khanna et al., 2015).

The decreasing order of ECR for the carcinogenic elements follows the similar trend for both adults and children: Cr(VI) >Cd > Ni > As > Pb. The highest ECR for Cr(VI) with concentration smaller than other metals excluding As, is because of its high inhalation unit risk, ranging from 6 to 1000 times compared to other metals taken into account. Pb and As for adults and Pb, Ni, As and Cd for children are under permissible limit. The cancer risk value for adults is being exceeded by the Cr(VI) (10.6×10^{-6}), Cd (3.43×10^{-6}) and Ni (1.24×10^{-6}) whereas in case of children Cr

Table 4
Excess Cancer Risks (ECR) of carcinogenic elements in PM_1.

	Carcinogen group	C (μg/m³)	[a] IUR (μg/m³)⁻¹	Excess cancer risk	
				Adults	Children
Pb	B2 (Probable human carcinogen)	2.30E − 01	0.000012	1.55E − 07	3.86E − 08
Ni	A (Human Carcinogen)	9.20E − 02	0.00024	1.24E − 06	3.09E − 07
As	A (Human Carcinogen)	2.40E − 03	0.0043	5.78E − 07	1.44E − 07
Cd	B1 (Probable human Carcinogen)	3.40E − 02	0.0018	3.43E − 06	8.57E − 07
[b] Cr(VI)	A (Human Carcinogen)	1.57E − 02	0.012	1.06E − 05	2.64E − 06
			Total ECR	1.60E − 05	3.99E − 06

C is the ambient concentration; IUR is inhalation unit risk factor.
[a] Values taken from IRIS (Integrated Risk Information System).
[b] Cr(VI) concentration is 1:7 of total Cr concentration.

(VI) (2.64×10^{-6}) exceeds the permissible cancer risks. The total average ECR for adults and children are 16.1×10^{-6} and 3.99×10^{-6} respectively which signifies higher cancer risk persists for adults than children. A similar study at Ulsan city, South Korea reported cancer risk due to PM_1 bound metals about 20.4×10^{-6} where, also Cr(VI) and Cd contributing to cancer risks were higher than other metals (Hieu and Lee, 2010). Since the value is extending the range limit of (10^{-6}), so the contamination does produce significant carcinogenic risk, although more studies on PM_1 bound metals are needed to confirm the significant cancer risks.

However, despite there are some uncertainties about the computed health risk results, like the uncertainties of models, exposure parameters and metals toxicity values, this assessment model is powerful way for assessing the human health risk due to the exposure to heavy metals in the environment.

4. Conclusion

The annual data set available for IIT Kanpur campus reveals daily average PM_1 concentration as 102.46 ± 35.9 μg/m^3 with the levels highest during winter time and lowest during monsoon season. Daily mean concentration trends were dominated by metals of crustal origin: Ca > Fe > Mg > Zn > Pb > Cu > Cr > Ni > Se > Cd > V > As. The contamination level assessment was done by using pollution indices, Geo-accumulation Index. The results showed wide range of contamination levels for different metals. Ca, Fe and Mg exhibited non-contamination, V and Cd exhibited moderate contamination and Zn, As, Cd, Pb, Se, Ni and Cu exhibited heavy to extreme contamination.

The exposure pathway which exhibited highest level of risk to adults and children exposed to metals in PM_1 was ingestion followed by dermal contact and inhalation. Health risk analysis showed among the metals considered Pb, Cr and Cd (HI > 1) have the potential to cause non-carcinogenic risks to children. In contrast, values for adults are well under safe limit (HI < 1) indicating no non carcinogenic risk from heavy metals. The potential carcinogenic health risk related to carcinogen heavy metals followed the similar trends for both adults and children, Cr(VI) >Cd > Ni > As > Pb. The Total excess cancer risks were found to be well above the acceptable level (10^{-4}–10^{-6}) for both adult and children. As it was the first attempt to assess exposure to heavy metals and uncertainties could not be neglected. Further studies should lay down exposure parameters which could contemplate local human activities mode to give more authentic risk assessment outcomes.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2015.12.039.

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