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Chemical fractionation and health risk assessment of particulate matter-bound metals in Pune, India

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Abstract The present study deals with the assessment of sequential extraction of particulate matter (PM)-bound metals and the potential health risks associated with them in a growing metropolitan city (Pune) of India. The average mass concentration of both $PM_{2.5-10}$ and $PM_{2.5}$ exceeded the National Ambient Air Quality Standards. Significant seasonal variation in mass concentration was found for both size fractions of PM with higher values in winter season and lower in monsoon. Chemical species of the studied trace metals in PM exhibited significant differences, due to difference in sources of pollution. Metals such as Cd, Pb, and Cr in both size fractions and Zn and Co in fine fraction were more efficiently extracted in mobile fractions showing their mobile nature while Ni and Fe showed reduced mobility. Fe showed the highest concentrations among all the analyzed elements in both coarse ($PM_{2.5-10}$) and fine ($PM_{2.5}$) PM, while Cd showed least concentration in both size fractions. PCA identified industrial emissions, vehicular activity, coal combustion, diesel exhaust, waste incineration, electronic waste processing, constructional activities, soil, and road dust as probable contributors responsible for the metallic fraction of PM. All the metals showed varying contamination in PM samples. The contamination was higher for fine particles than coarse ones. The average global contamination factor was found to be 27.0–34.3 in coarse and fine PM, respectively. The hazard quotient (HQ) estimated for Cd, Co, and Ni (both total and easily accessible concentrations) exceeded the safe level (HQ $= 1$), indicating that these metals would result in non-carcinogenic health effects to the exposed population. The HQ ranged from 9.1×10^{-5} for Cu (coarse) to 8.3 for Ni (fine) PM. The cancer risk for Cd, Ni, and Cr in both sized PM were much higher than the acceptable limits of USEPA.

Keywords PM_{10} · $PM_{2.5}$ · Metals · Sequential extraction · Health risk assessment

Introduction

Particulate pollution in most of the Indian cities is increasing at a fast pace due to increasing vehicle fleet, urbanization, and industrialization. The World Health Organization (WHO) ranks particulate pollution as the 13th leading cause of mortality worldwide, and about 3.7 ± 1.0 million deaths are attributed annually to fine particulate matter (Anderson et al. 2012; Silva et al. 2013). A recent study by global burden of diseases reported 3.2 million deaths per year and 76

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million years of healthy life lost by ambient fine particulate matter (PM) (Cui et al. 2015). Globally, millions of people suffer from various respiratory problems and other diseases attributed to the presence of toxic substances and biological components present in the particulate matter (Mohanraj and Azeez 2004). PM refers to a suspension of solid, liquid, or a combination of both solid and liquid particles in the air consisting of a variety of components such as organic compounds, metals, acids, soil, and dust (Rai 2015). Components like transition metals, polycyclic aromatic hydrocarbons, and biological agents (bacteria and fungi) are considered to be associated with PM, either through an integral part of the particles or through adherence to the particles (Osornio-Vargas et al. 2003). Among known pollutants, metals are considered as deleterious pollutants because of their toxicity, persistency, and non-degradable nature in the environment (Aina et al. 2009; Mohiuddin et al. 2010; Villanueva and Raposo 2013). These potentially harmful elements (PHEs) are released by both natural and anthropogenic sources, viz., crustal materials, construction activities, road dust, motor vehicle emissions, incineration, industrial emissions, and coal and oil combustion (Shah and Shaheen 2010). Exposure to metals in the air is responsible for causing a number of human health effects, varying from respiratory and cardiovascular effects to various types of cancers and damage of essential organs. Significantly adverse health effects occur due to exposure to particle-bound metals even at low concentration (Geiger and Cooper 2010). It is hypothesized that PM-induced toxicity may be due to the changes in the redox status of the cells by reactive oxygen species (ROS) generated by the interaction of PM within lung cells and macrophages (Wang et al. 2013). Metals can exert their toxic effects mainly by two processes. They can directly damage tissues or cells or they can substitute for metals required by our body. Fenton active metals like Fe, Cu, Cr, and V undergo redox cycling and generate free radicals. However, redox inactive metals like Cd, Pb, and Hg are unable to go through Fenton or Heber–Weiss reaction, but they too produce oxidative stress as they deplete cells major antioxidants resulting in the production of ROS such as superoxide, hydrogen peroxide, and OH radicals (Stohs and Bagchi 1995). For example, Cd inhibits the activity of antioxidants such as catalase (CAT) and superoxide dismutase (SOD) via binding to the thiol (–SH) group, whereas significant inhibition in enzymatic activity of glutathione (GSH) and SOD has also been reported after Pb exposure (Birben et al. 2012). In addition to this, Pb replaces Zn, a cofactor in many enzymes leading to the inactivation of such enzymes (Ercal et al. 2001). Many recent studies support the significant role of metals in the toxicity of PM (Das et al. 2015; Satsangi et al. 2014; Mukhtar and Limbeck 2013; Li et al. 2013; Sadovska 2012). Strong evidences produced by these studies indicate that metals associated with PM contribute to its health effects.

Previous studies have focused on the investigation of the total metal contents in PM which is a poor indicator of metal mobility, bioavailability, and toxicity (Okoro et al. 2012). The quantification of the specific form of metal is necessary because its origin, mode of occurrence, bioavailability, geochemical transport, solubility, potential mobility, and metal biogeochemical cycles largely depend on its physicochemical speciation (Villanueva and Raposo 2013; Canepari et al. 2010). Sequential extraction is a valid tool for assessing mobility and bioavailability of particle-bound metals. Further, fractionization of total metal content by sequential extraction improves our knowledge on the identification of emission sources of PM-bound metals and their impact on health and environment (Canepari et al. 2010). Various sequential extractions, viz., (1) based on Tessier's procedure, (2) based on BCR procedure, (3) based on Chester's procedure schemes, and (4) others, have been recently used for airborne particles. However, there are some limitations associated with these schemes such as (1) the complex nature of PM, (2) the small mass of the collected samples on filters, and (3) the choice of reagent and extraction conditions, which make it difficult for comparison of reported results from the different geographical locations (Kumar et al. 2008; Schleichera et al. 2011; Canepari et al. 2010).

Pune, the cultural and educational capital of the state of Maharashtra, is subjected to particulate pollution from various sources such as service industries, vehicular traffic, construction activities, and more recently, information technology and biotechnology. The industrial area covers nearly 10,000 industries that include TATA, Bajaj, Thermax, and L&T (Sonaje et al. 2013). According to census 2011, Pune has a population of 9.43 million, out of which 61% lives in urban areas of Pune and remaining 39% population lives in rural areas (Mundhe and Jaybhaye

2014). Rapid rise in urbanization and population has tremendously increased vehicular count by 54% in the city from 16,22,675 in 2008 (Gidde and Sonawane 2012) to 29,83,749 in 2015 (Times City, December 9, 2015). The adverse consequence of these sources is the deterioration of air quality of Pune. Studies on particulate matter-bound metals reported from this city are scanty (Yadav and Satsangi 2013), and no studies are reported on sequential extraction, contamination, and health risk assessment of PM, clearly pointing to the existence of a knowledge gap from this area. Thus, the main objectives of this paper are as follows: evaluation of air quality of Pune in terms of PM_{10} and $PM_{2.5}$ levels; chemical fractionation (sequential extraction) of metals in both coarse and fine PM; identification of possible sources of metals by principal component analysis (PCA); assessment of health risk associated with the studied metals in terms of hazard quotient (HQ) and cancer risk.

Materials and methods

Site description

Pune (18°32′N, 73°51′E) is situated at the elevation of ~560 m above sea level, in the Sahyadri Hills near West Coast of India. Pune has a tropical wet and dry climate with average temperatures ranging between 15 and 35 °C. The city is expanding at a faster rate in terms of vehicular population, industrialization, and urbanization. The presence of IT hubs and various educational centers lead to the immigration of people from other states (Gidde and Sonawane 2012). The economic activity on the outskirts of the city, particularly in the Pimpri–Chinchawad region, has a direct impact on the city of Pune. These factors together with geographical location contribute to the high loads of atmospheric pollution in terms of PM coming mainly from anthropogenic sources (Fig. S1). The sampling was carried out at the roof of a building (12 m above the ground) at Hadapsar, Pune. The sampling site is surrounded by a number of small-scale and large-scale industries (Pragati paints and allied products, Impak steel industries Pvt. Ltd., Union steel industries etc). In addition to this vehicular traffic, biomass burning, waste dumping, and soil dust are major sources of PM at this site.

Sample collection and gravimetric analysis

Twenty-four-hour samples of PM_{10} and $PM_{2.5}$ were collected on PTFE filters (Whatman, 47 mm), with fine particulate medium-volume dust sampler (APM 550, Envirotech). For PM_{10}, a total of 108 samples (winter: 40; summer: 36; monsoon: 32) and for $PM_{2.5}$ a total of 120 samples (winter: 44; summer: 40; monsoon: 36) were collected during the entire study period. On the basis of significant differences from the rest of the dataset, 5–7% samples have been removed as outliers. To check the consistency in the flow rate (16.6 L/min), daily flow rate calculations were made. In order to reduce the possibility of contamination, Teflon-coated tweezers were used for handling the filters. The loss of semi-volatile constituents was minimized by refrigerating the collected samples at about 4 °C (Li et al. 2015a). Prior to weighing, filters were conditioned for 24 h under controlled conditions (temperature: 25 ± 1 °C, relative humidity: 40 ± 5%) before and after the sampling. Samples were then weighed using an analytical balance (Sartorius, BSA224S-CW), and the total PM mass was gravimetrically determined by subtracting the initial mass of the blank filter from the final mass of the collected filter paper.

Air quality index (AQI) was calculated (Eq. 1) for the mass concentration (24 h) of PM_{10} and $PM_{2.5}$ for the entire study period.

$$\mathrm{AQI} = \frac{\text{Mass concentration (24 h)}}{\text{24 h NAAQS Standard}} \times 100 \tag{1}$$

The index range obtained from the formula of AQI is divided into five categories, i.e., 0–33 (very poor air quality: VPAQ), 34–66 (good air quality: GAQ), 67–99 (fair air quality: FAQ), 100–149 (poor air quality: PAQ), and 150 or greater (very poor air quality: VPAQ).

Sequential extraction and chemical analysis

In this study, a four-step extraction procedure based on Chester's procedure (Richter et al. 2007) was applied to fractionate the particulate matter-bound trace metals into four fractions; water-soluble (F1), environmentally mobile (F2), bound to carbonates and oxides (F3), and organic and refectory associated or residual fraction (F4). The filter paper was cut into pieces and was placed into conical flask. For F1 fraction, 10 mL of milli-Q water was added to the flask, which was then ultra-sonicated for 1 h followed by centrifugation. To the residue, 25 mL of CH_3COONH_4 (1 M) (pH 7) solution was added. After shaking the mixture for 1.5 h, it was centrifuged for 15 min. The supernatant was decanted into polypropylene bottles (F2), and the residue was agitated for 6 h after the addition of 25 mL of $NH_2OH{\cdot}HCl$ (1 M) + 25% (v/v) CH_3COOH solution. The mixture was then again centrifuged for 15 min to separate the supernatant and considered as F3. 10 mL of HNO_3, 2 mL of HF, and 1 mL of H_2O_2 were added to the residue and were digested by microwave oven followed by evaporation on hot plate. The final volume was diluted to 25 mL and labeled as F4. All four fractions were stored in a refrigerator at 4 °C until analysis to quantify the presence of Cu, Mn, Zn, Cd, Fe, Co, Ni, Cr, and Pb by inductively coupled plasma atomic emission spectroscopy (ICP-AES; ARCOS, Spectro, Germany). The calibration of ICP-AES was performed by using multi-element standard reference solution (1.11355.0100, Merck-1000 mg/L). A calibration curve was plotted from the known standard solutions (0, 0.05, 0.1, 0.5, 1, and 10 mg/mL standards), prepared by step dilution of reference solution. Dilute HNO_3 was used as blank and for the dilution of standards. Metal analysis of all the four fractions was done in triplicate, and the concentration was reported as the average of triplicates.

Quality control

Calibration of weighing balance (internal as well as external) was done each time before weighing the samples. Periodic cleaning of the sampler was done to make it free from particles and dust. In order to minimize re-entrainment biases to mass and elemental concentration, frequent cleaning and greasing of inlet impaction surfaces was done. To avoid error due to loss of fibers or particles from the filters, filters were carefully handled from pre-weighing, through sampling to post-weighing. Collected samples were removed and transferred soon after sampling into sample cassettes and were stored in airtight containers in refrigerator till the analysis. Field blanks and filter blanks were analyzed with each batch of samples using the same procedure as for the samples to check the field blank ground contamination. There was no difference between the filter and the field blanks, and the metal concentration in both of them was below detection limit. Recovery efficiencies (%) of metals were calculated by spiking the samples (15%) with known metal concentration. Table S1 (supporting information) shows the detection limit and recovery rate of metals in PM samples.

Meteorological parameters

Meteorological parameters such as relative humidity, temperature, wind speed, and direction were also recorded during the study period along with PM sampling because they may affect mass concentration of PM in the atmosphere. These meteorological parameters were measured by an automatic weather station (Envirotech-WM 271) and are given in Table S2 (supporting information).

Health risk assessment

Risk assessments can provide a great deal of information for understanding the PM-related health effects. Epidemiological studies have demonstrated a strong positive association between airborne PM and induction of serious adverse health effects (de Kok et al. 2006; Wiseman 2015). In order to evaluate the human health risk assessment associated with particulate matter-bound metals, health risk assessment models from USEPA were adopted. Exposure to these metals can occur through inhalation, ingestion, or by dermal contact, but in this study only inhalation route is considered. The average daily dose (A_{DD}) through inhalation was calculated according to Eq. 2 (USEPA 1992; Kushwala et al. 2012).

$$A_{\mathrm{DD}} = \frac{C \times \mathrm{InhR} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}} \qquad (2)$$

where C is the concentration (μg/m^3) of contaminants in air, InhR is the average inhalation rate (15.3 m^3/d), ED is the exposure duration which was assumed as 15 years, BW stands for body weight (60 kg), and AT is the average exposure time (365 × 15). The non-carcinogenic risk associated with the metals was calculated in terms of hazard quotient (HQ) which is the ratio of intake of a substance and the reference dose at which no adverse effects are expected. Hazard refers to the capacity of a specific agent to produce a particular type of adverse health effect in humans and other animals or environmental effect (USEPA 1995). It is the ratio of the time-weighted exposure concentration for a given metal to its reference concentration (Rfc) or other appropriate toxicity value and is calculated by Eq. 3 (Li et al. 2015a; USEPA 1989). For inhalation exposure, Rfc values for the metals like Cr, Ni, Mn, Co, and Cd were taken from USEPA while there are no reported USEPA Rfc values for metals, viz., Cu, Zn, Fe, and Pb. Therefore, reference dose (Rfd) values for oral exposure of these metals are applied in this study with the assumption that after inhalation, the metals would result in similar health effects as if they had been ingested (Wang et al. 2015).

$$\mathrm{HQ} = \frac{A_{\mathrm{DD}}}{\mathrm{Rfc}\,(\mu\mathrm{g})} \tag{3}$$

The non-carcinogenic effects are only possible when $\mathrm{HQ} > 1$, and if the calculated HQ is less than one, no adverse non-cancerous health effects are expected. Generally, larger HQs indicate greater levels of concern.

Currently, in India, lung cancer is the fourth largest cause of cancer mortality after cervical, uterus, breast, lip, and oral cancers accounting for nearly 8% of all cancer related deaths in the country. Many metals have been tested for carcinogenicity and are potential agents in the toxicity of ambient PM. Lifetime cancer risk (R_{ic}) for four carcinogens (Cr, Ni, Cd, and Pb) was estimated by corresponding unit risks (URs) defined by US EPA, in Eq. 4 (USEPA 2009; Fang et al. 2013).

$$R_{\mathrm{ic}} = \frac{C \times \mathrm{ED} \times \mathrm{UR}}{70\,\mathrm{years}} \tag{4}$$

where C is the concentration of contaminants in air, ED is the exposure duration, UR is the unit risk, and 70 years is the average life.

Statistical analysis

To identify the nature of probable common sources of metals, principal component analysis (PCA) was applied on the total metal concentration of both PM_{10} and $\mathrm{PM}_{2.5}$, by using SPSS (SPSS, PC16 package). The principal components extracted by this method explaining the majority of variance of the data matrix are qualitatively interpreted as possible sources. After varimax rotation, the factors with eigenvalues greater than one were considered to obtain final factor matrix. A factor loading of >0.5 was considered in this study to assign a probable source to a principal component, present at this site.

Assessment of metal contamination

The assessment of metal contamination in PM provides a measure of degree of contamination of metals in environment with respect to its retention time. It is given by means of individual contamination factor (ICF) and global contamination factor (GCF) (Moses and Orok 2015; Naji et al. 2010). ICF is classified into four groups, $\mathrm{ICF} < 1$ means low contamination; $1 \le \mathrm{ICF} \le 3$ means moderate contamination; $3 \le \mathrm{ICF} \le 6$ indicates considerable contamination; and $\mathrm{ICF} > 6$ indicates very high contamination. It is a single-element index, calculated as follows:

$$\mathrm{ICF} = C_{\mathrm{nonresistant}}/C_{\mathrm{resistant}} = C\,(\mathrm{F1} + \mathrm{F2} + \mathrm{F3})/C\mathrm{F4}$$

where $C_{\mathrm{resistant}}$ stands for the residual metal concentration which is usually unavailable for humans and plants. $C_{\mathrm{nonresistant}}$ is the concentration of metals in the first three fractions, which become available to human body and or plants, on changing the pH. The sum of ICFs of all the elements in a sample gives the global contamination factor.

$$\mathrm{GCF} = \sum \mathrm{ICF}$$

Results and discussion

Mass concentration

The particulate matter concentrations varied from 50–402 μg/m^3 for PM_{10} and 29–338 μg/m^3 for $\mathrm{PM}_{2.5}$ with an average of 122 ± 62 and 81 ± 50 μg/m^3, respectively. For both PM_{10} and $\mathrm{PM}_{2.5}$, the values are 2 times higher than the annual Indian National Ambient Air Quality Standard (60–40 μg/m^3, respectively) as prescribed by the Central Pollution Control Board (CPCB) (NAAQS 2009) and 2.4–3.3 times higher than the respective WHO air quality guidelines (50 μg/m^3 for PM_{10} and 25 μg/m^3 for $\mathrm{PM}_{2.5}$) (WHO 2006). The results of the present study revealed that the level of PM_{10} and $\mathrm{PM}_{2.5}$ is of the major concern because their levels exceed the permissible limits. According to AQI data, the average air quality of Pune in terms of PM_{10} and $PM_{2.5}$ was found to be poor. In case of PM_{10}, 16.1% of the samples showed very poor air quality (VPAQ), 48.4% samples showed poor air quality (PAQ), 25.8% samples showed fair air quality (FAQ), and only 9.7% samples depicted good air quality (GAQ), while in case of $PM_{2.5}$, the percentage contribution was 31, 34.5, 24.1, and 10.3% for VPAQ, PAQ, FAQ, and GAQ, respectively (Fig. S2—supporting information). The average ratio of $PM_{2.5}/PM_{10}$ mass concentration in this study ranged from 0.51 to 0.83 with an average of 0.70, i.e., PM_{10} is composed of about 70% of $PM_{2.5}$ particles. This indicates the dominance of $PM_{2.5}$ particles in the collected samples.

On applying the ANOVA, significant seasonal variation ($p = 0.05$) in the mass concentrations of both $PM_{2.5}$ and PM_{10} has been found with declining trend from winter to monsoon [winter (November–February) > summer (March–May) > monsoon (June–September)] (Fig. 1). The concentrations of PM_{10} and $PM_{2.5}$ in the winter season were about ~1.3 and ~2.3 times higher than the concentrations observed during summer and monsoon seasons, respectively. The higher PM concentrations in the winter season may result from various factors such as low mixing level, persistent temperature inversions, higher heating load, and the reduced dispersion of local sources during this period (Table S2) (Xu et al. 2008; Kothai et al. 2011). In addition to this, the condensation of semi-volatile species in air causes high PM concentration in winter as compared to the summer and winter (Rogula-Kozłowska et al. 2014). Lower concentration of PM_{10} and $PM_{2.5}$ in monsoon is due to the washout of particles by precipitation.

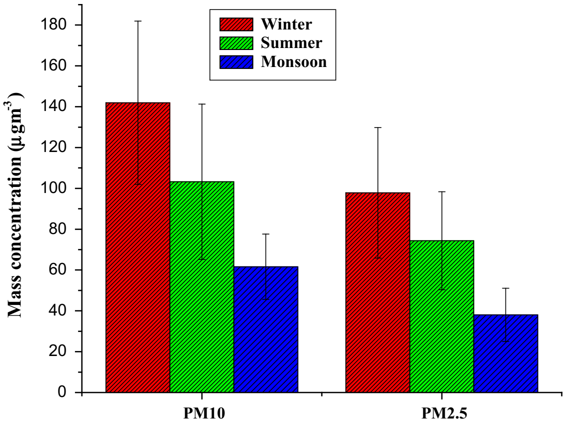

Fig. 1 Seasonal variation in mass concentration of PM_{10} and $PM_{2.5}$ in Pune

In order to identify the role of transport patterns of air masses and the potential sources arriving at the sampling site during different seasons, seven-day backward air trajectories, carried out at height of 500 m, were calculated using the web version of National Oceanic and Atmospheric Administration (NOAA) Hybrid Single Particle Lagrangian Integrated Trajectories (HYSPLIT) model (Pipal et al. 2014). As inferred from the trajectory analysis (Fig. 2a), elevated PM concentrations in winter were clearly associated with both long-range transport and local air masses carrying the dust and aerosol particles, coming to the sampling site from Pakistan, Afghanistan, Arabian Sea, Bay of Bengal, UP, MP, Rajasthan, Jharkhand, West Bengal, and neighboring regions of Pune, whereas during the summer season, the long-range transport of air masses seems approaching to the study site from Pakistan, Afghanistan, Arabian Sea, and Bay of Bengal. In addition to this, less frequent local air parcel episodes were also observed during this period (Fig. 2b). The low levels of PM during monsoon period may be attributed to winds arriving from Arabian Sea with lesser extent of anthropogenic and industrial activities (Fig. 2c).

Metal concentration

Characterization of PM in terms of metal composition provides interesting data on specific emission sources and the potential impact on human health and environment (Canepari et al. 2009). The metal concentration in coarse particles (CP) ($PM_{10-2.5}$) was obtained by subtracting $PM_{2.5}$ (fine particulates—FP) from PM_{10}. Table 1 represents total concentration of metals in PM samples obtained by simple summation of the metal concentrations of the four extraction steps. Fe showed the highest concentrations among all the elements analyzed in both CP and FP, followed by Ni and Zn in FP and Mn in CP, while Cd showed least concentration in both the size fractions. The concentration of metals in CP and FP were in the order Fe > Mn > Zn > Cr > Co > Cu > Pb > Ni > Cd and Fe > Ni > Zn > Cr > Pb > Co > Cu > Mn > Cd, respectively. The metals of crustal origin (Fe and Mn) were more dominant in CP, whereas the metals of anthropogenic origin (Zn, Cd, Pb, Ni, and Cr)

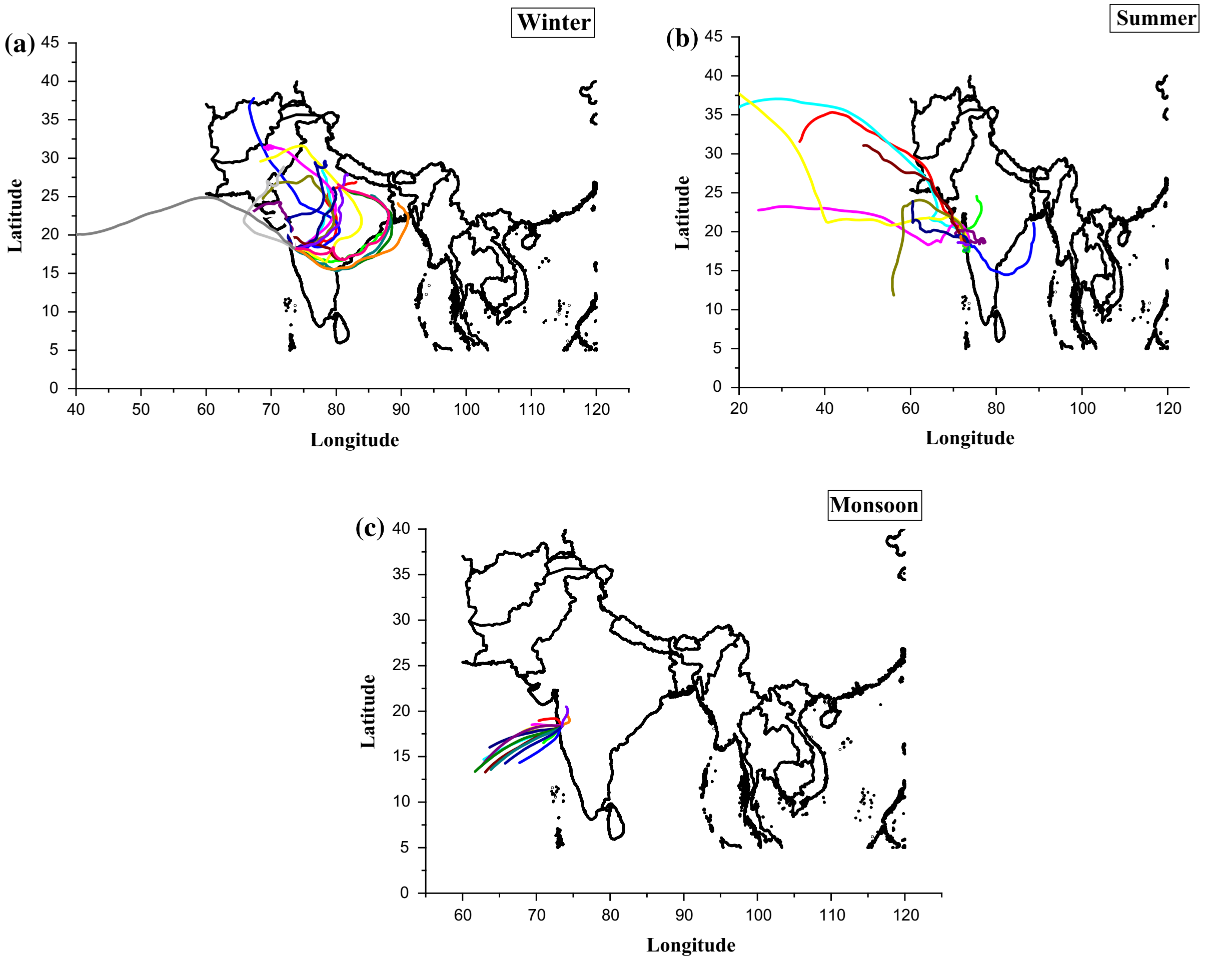

Fig. 2 Seasonal air mass backward trajectory analysis for 7 days ending at Pune at 500 m amsl heights

were more concentrated in FP. Probable main sources of these metals at this site are metallurgical and pigment activities, road transport, constructional activities, soil and road dust, biomass combustion, steel works, and various medium-scale and small-scale industries present which was previously discussed in Sect. 2. In addition to this, the industrial activities at the outskirts of this city particularly from the Pimpri–Chinchawad and Bhosari located at about 22 and 26 km from the site may also contribute to the metal concentration. The local transport of pollutants is also supported by the trajectory data (Fig. 2a, b). All metals showed a clear seasonal trend of winter > summer > monsoon except Fe and Mn which exhibited the trend of summer > winter > monsoon in both size fractions. The higher concentration of metals during winter may be due to lower wind speed (1.35 km/h) and thermal inversion which leads to the poor dispersion of particle-bound metals from the local sources during this season (Bathmanabhan and Madanayak 2010). Another possible reason of high concentration of these metals may also be due to their long-range transport (Fig. 2a). For example, metals like Cd and Pb reside in the atmosphere for many days, therefore likely to be transported to local, regional, and global scale (Dey et al. 2014). The high concentration of Fe and Mn (mainly from crustal origin) in summer may be attributed to the strong wind speed (17.29 km/h) and lower relative humidity (56.9%), favoring the atmospheric dust re-suspension (Khillare and Sarkar 2012; Bourotte et al. 2011). The lower concentration of metals during the monsoon may be due to strong winds and higher relative humidity, which results in higher dilution and settling of the metal-bound particles on the ground. The

Table 1 Average concentration of metals (μg/m^3) in terms of their extractability by different reagents

	F1	F2	F3	F4	Total
Fine ($N = 111$)					
Cu	0.040 ± 0.03	0.025 ± 0.02	0.106 ± 0.08	0.070 ± 0.04	0.240 ± 0.14
Zn	0.107 ± 0.07	0.087 ± 0.07	0.195 ± 0.11	0.148 ± 0.07	0.538 ± 0.28
Fe	0.060 ± 0.10	0.097 ± 0.17	0.675 ± 1.09	1.368 ± 1.20	2.200 ± 1.20
Pb	0.055 ± 0.02	0.102 ± 0.09	0.037 ± 0.01	0.091 ± 0.09	0.285 ± 0.23
Cd	0.033 ± 0.02	0.026 ± 0.01	0.018 ± 0.00	0.021 ± 0.00	0.099 ± 0.04
Mn	0.034 ± 0.03	0.049 ± 0.06	0.052 ± 0.05	0.090 ± 0.06	0.225 ± 0.24
Co	0.067 ± 0.04	0.082 ± 0.05	0.051 ± 0.04	0.066 ± 0.07	0.265 ± 0.16
Cr	0.055 ± 0.04	0.064 ± 0.04	0.113 ± 0.10	0.087 ± 0.05	0.319 ± 0.18
Ni	0.051 ± 0.06	0.026 ± 0.02	0.163 ± 0.12	0.390 ± 0.30	0.630 ± 0.50
Coarse ($N = 102$)					
Cu	0.003±0.00	0.016 ± 0.00	0.075 ± 0.04	0.113 ± 0.07	0.206 ± 0.09
Zn	0.023 ± 0.02	0.059 ± 0.08	0.041 ± 0.04	0.203 ± 0.10	0.325 ± 0.01
Fe	0.233 ± 0.27	0.375 ± 0.49	1.699 ± 1.25	2.795 ± 1.52	5.103 ± 0.95
Pb	0.020 ± 0.01	0.066 ± 0.03	0.024 ± 0.01	0.037 ± 0.01	0.147 ± 0.02
Cd	0.053 ± 0.03	0.020 ± 0.01	0.004 ± 0.00	0.012 ± 0.01	0.088 ± 0.00
Mn	0.045 ± 0.03	0.062 ± 0.05	0.106 ± 0.06	0.182 ± 0.10	0.395 ± 0.11
Co	0.031 ± 0.02	0.021 ± 0.01	0.105 ± 0.10	0.064 ± 0.05	0.222 ± 0.02
Cr	0.037 ± 0.02	0.094 ± 0.07	0.064 ± 0.04	0.046 ± 0.03	0.241 ± 0.09
Ni	0.017 ± 0.01	0.007 ± 0.01	0.027 ± 0.01	0.074 ± 0.06	0.124 ± 0.09

F1 = water-soluble fraction,
F2 = environmentally mobile fraction,
F3 = fraction bound to carbonates and oxides, and
F4 = organic and refectory associated or residual fraction

lower concentration of the metals in monsoon may also be due to the scavenging of the particles containing metal by precipitation.

Fractionation and source identification of metals in PM

The chemical fractionations of metals provide more valuable and reliable information about the potential toxicity, health risks, and source identification of metal-bound particles. The results obtained from the sequential extraction provide an interesting insight about the variability of metals associated with two particle sizes. Results obtained from the four-step sequential extraction procedure on PM samples are presented in Table 1. The percentage distribution of metals in different fractions is shown in Fig. 3a, b. The chemical bonding of Cd, Pb, and Cr resulted into their strong association with the mobile fraction (F1 + F2) of both particle sizes. About 83–66% of Cd, 59–55% of Pb, and 54–38% of Cr in CP and FP, respectively, are concentrated in this fraction. Previous studies have also reported higher concentration of Cd (53–83%) and Pb (45–94%) in mobile fractions (Kumar et al. 2008; Richter et al. 2007). The metals associated with this fraction are more mobile and show higher accessibility, thus possessing higher potential to cause adverse effects (Mbengue et al. 2015). A smaller amount of Cd (13% in CP and 18% in FP) was also associated with the organic and refractory associated fraction while 16% (FP) was bound to carbonates and oxides. A significant amount of Pb was also found in F4 (32% in FP and 25% in CP) and the lower percentages were found in the F3 fraction of CP (13%) and FP (16%), respectively. The metals associated with F3 become available when the oxidation–reduction potential of the matrix increases; therefore, they are also considered as easily accessible (Feng et al. 2009). Ni and Fe were mainly found to be accumulated in F4 (residual) fraction. About 59–62% of Ni and 55–62% of Fe for CP and FP, respectively, are accumulated in the F4 fraction. In addition to this, 23–26% of Ni and 33–31% of Fe in CP and FP were found in the F3 fraction. These two metals followed the trend F4 > F3 > F1 + F2. The lowest concentration of these two metals was found in the mobile fraction (F1 + F2). However, these two metals are less mobile, but may still pose potential health and environment risk because of their presence in the F3 fraction. Zn and Co in FP were equally distributed in

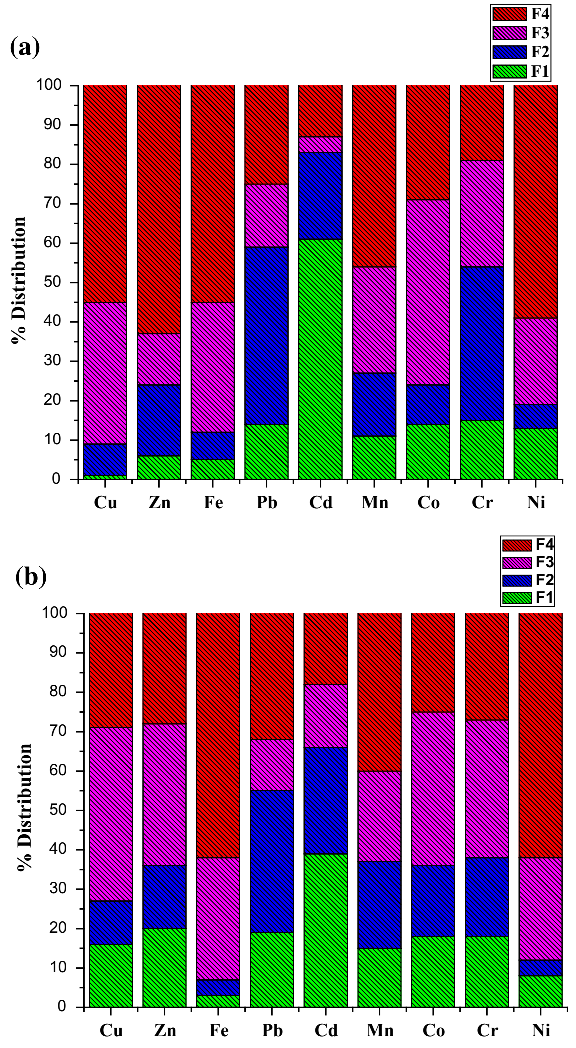

Fig. 3 Percent distribution of metals in various sequentially extracted steps, **a** coarse, **b** fine

F3 (36–38%) and F1 + F2 (36–37%) fractions, and about 29–25% of them was found in F4 fraction. In case of CP, Zn was mainly concentrated in F4 (62%) followed by F1 + F2 (25%), while Co was accumulated in significant percentage in all the fractions with highest percentage in F4 fraction. Cu partitioning in different fractions followed the order: $F4 > F3 > F1 + F2$ in CP and $F3 > F4 > F1 + F2$ in FP. High amount of Cu in the fourth fraction, i.e., F4 (residual and organic fractions), indicated its reduced mobility. The association of Cu with F3 and F4 can be explained by the fact that acid-soluble and Fe–Mn oxides of Cu in PM show strong specific covalent interaction with organic matter because the high stability constant of organic Cu compounds favors its complex formation with organic matter (Li et al. 2013; Ladigbolu 2014). Distribution of Mn in FP was very similar and followed the trend $F4 > F1 + 2 > F3$ while in CP, Mn followed the order $F4 > F3 = F1 + 2$ and $F4 > F3 > F1 + 2$, respectively.

Table 2 depicts the season-wise PCA of metals in CP and FP. In winter, PCA identified three factors for CP and four factors for FP with a total variance of 73.4 and 80.9% respectively. In case of CP, factor 1 with high loading of Fe, Pb, and Cd explained 26.6% variance and may be attributed to electronic waste processing at this site (Owoade et al. 2015). 23.4% of variance was also observed in factor 2 with high loading of Mn and Ni, and moderate loading of Pb and Co in winter. This factor possibly represents emission from coal combustion (Tian et al. 2015) and factor 3 (20.4%) with loading of Zn, Co, and Cr, which may be attributed to vehicular activities (Kar et al. 2010). In FP, factor 1 explaining 33.2% variance with loading of Cu, Zn, Co, and Cd may be attributed to an industrial origin (Kar et al. 2010; Chelani et al. 2010; Kothai et al. 2008). Factor 2 with 16.9% variance with high loading of Fe and Ni in winter is likely to be related to construction activities (Pant and Harrison 2012). Factor 3 (15.5%) with high loading of Cu and Cd and lower loading of Pb can probably be assigned to coal combustion (Meena et al. 2015). Factor 4 accounted for 15.2% variance in winter and showed high loading of Pb and Mn indicating the probable influence of re-suspended road dust (Thorpe and Harrison 2008). Although unleaded gasoline is commonly used in India, Pb still persists in road dust from earlier vehicular exhaust emissions due to its longer residence time in environment (Kulshrestha et al. 2009; Khanna et al. 2015; Meena et al. 2015). In summer season, three factors were identified by PCA for each CP and FP explaining a variance of 79 and 84.4%, respectively. In CP, factor 1 with a variance of 43% was loaded with Cu, Co, Cr, Zn, and Fe and suggests a probable mixed source from industrial emissions and soil dust (Kulshrestha et al. 2009; Khare and Baruah 2010). Factor 2 (19.6%) was loaded with Pb and Ni, and factor 3 (16.4%) was loaded with Cu possibly attributed to emissions from diesel exhaust and solid waste incineration, respectively (Lin et al. 2015; Owoade et al. 2015). In case of FP, factor 1 was loaded with Pb, Co, Cr, and Ni, likely to be assigned to the industrial emission (Kothai et al. 2008). Factor 2

Table 2 Season-wise principal component analysis (PCA) of metals in (a) coarse PM and (b) fine PM

	Factor	Cu	Zn	Fe	Pb	Cd	Mn	Co	Cr	Ni	% Variance	Eigen value	Probable source
(a)													
Winter	1	−0.86	0.12	**0.72**	**0.61**	**0.84**	−0.20	−0.16	−0.16	0.41	26.6	3.3	Electronic waste processing
	2	−0.08	−0.01	−0.07	**0.54**	0.11	**0.82**	**0.62**	0.00	**0.71**	23.4	2.4	Coal combustion
	3	0.15	**0.85**	−0.08	0.08	0.10	−0.26	**0.63**	**0.86**	0.04	20.4	1.6	Vehicular activities + soil dust
Summer	1	**0.77**	**0.84**	**0.87**	0.19	−0.06	0.52	**0.64**	**0.84**	0.49	43.1	5.1	Industries + soil dust
	2	0.46	0.40	0.07	**0.94**	0.08	−0.28	0.33	0.14	**0.68**	19.6	1.6	Diesel exhaust
	3	**0.53**	0.24	0.08	0.22	0.44	0.19	−0.03	−0.38	−0.39	16.4	1.2	Solid waste incineration
Monsoon	1	**0.83**	−0.08	**0.60**	**0.79**	−1.00	**0.72**	0.39	**0.88**	**0.87**	60.9	8.8	Industries + road + soil dust
	2	**0.55**	−1.00	**0.80**	**0.61**	0.09	**0.70**	**0.61**	0.48	0.49	39.0	1.2	Road and soil dust
(b)													
Winter	1	**0.88**	**0.90**	0.04	−0.15	**0.50**	0.36	**0.96**	0.30	0.29	33.2	3.5	Industrial origin
	2	0.06	0.25	**0.83**	0.18	−0.17	−0.37	0.14	−0.08	**0.84**	16.9	1.9	Construction activities
	3	**0.89**	0.07	−0.59	**0.65**	**0.92**	0.16	0.33	0.27	0.30	15.5	1.7	Coal combustion
	4	0.14	−0.14	0.04	**0.89**	0.13	**0.74**	0.10	0.16	−0.04	15.3	1.1	Re-suspended Road dust
Summer	1	0.23	0.18	−0.31	**0.52**	0.17	0.24	**0.61**	**0.93**	**0.82**	33.4	5.1	Industrial emission
	2	−0.17	0.00	−0.21	−0.10	**0.73**	−0.01	0.14	−0.84	0.19	27.2	2.1	Waste incineration
	3	0.29	**0.87**	**0.70**	0.42	−0.10	**0.72**	0.48	0.20	−0.09	23.7	1.2	Steel Industries + road dust
Monsoon	1	**0.71**	**0.77**	0.32	0.12	−0.05	−0.08	0.10	**0.68**	0.09	50.2	5.4	Vehicular traffic
	2	0.02	**0.72**	0.24	**0.70**	**0.74**	0.03	**0.73**	0.33	0.05	42.4	3.9	Industrial

Factor loading above 0.5 are denoted with bold explained 27.2% variance with high loading of Cd, which may be associated with municipal solid waste incineration at this site (Li et al. 2015; Tian et al. 2012). Factor 3 with higher principal loading for Zn, Fe, and Mn explained 23.7% of variance. These metals may be originated from steel industry and road dust from this site (Thurston et al. 2011; Srivastava and Jain 2007). A total variance of 100 and 94.6% was explained by two factors each for CP and FP, respectively, in the monsoon season. The factor 1 of CP explaining 60.9% variance was loaded with Cu, Fe, Pb, Mn, Cr, and Ni. This factor can probably be identified as a mixed source from industries and re-suspended road and soil dust. Factor 2 with a variance of 39% in monsoon of CP was loaded with Fe, Pb, Mn, Co, Ni, and Cu commonly attributed to windblown road and soil dust (Srivastava and Jain 2007). In case of FP, 50.2% variance was explained by first factor in monsoon with loading of Cu, Zn, and Cr which may be attributed to the vehicular traffic (Khillare and Sarkar 2012). Factor 2 with loading of Pb, Cd, Co, and Zn explained 42.4% variance, possibly assigned to the industrial emission (Shah et al. 2012).

Metal contamination

The computed results for individual and global contamination factor for metals are shown in Table 3. All the metals showed varying contamination in both size fractions of PM samples. The ICF ranged from 0.6–7.6 and 0.6–7.4 in case of CP and FP, respectively. The average ICF values of all metals except Cd and Cr were higher in FP than in CP. Samples of CP showed high contamination for Cd, considerable contamination for Pb, Cr, and Co, moderate contamination for Mn, and low contamination for Zn, Cu, Fe, and Ni. In case of FP, the contamination was high for Pb, considerable for Cu, Cd, Co, and Cr, moderate for Zn, Mn, and Ni, while Fe showed low contamination. Computed GCF value for CP and FP was found to be 27.0 and 34.3, respectively, which indicates that FP is more contaminated with the considered metals than CP samples.

Non-carcinogenic and carcinogenic risk assessments

The hazards of metals for human health are well known (Valavandis et al. 2008). The non-cancer risk assessment is designed to measure the threshold at which daily health effects occur. Non-carcinogenic risks associated with inhalation exposure to particulate matter-bound trace elements (determined for both water-soluble and total metal concentrations) were calculated for both CP and FP samples and the average values in terms of hazard quotient (HQ) are given in Table 4. Considering total concentration of a metal (TMC = F1 + F2 + F3 + F4), HQ value of four metals (i.e., Cd, Co, Mn, and Ni) exceeded the safe level (HQ = 1), but if the easily accessible (F1 + F2 + F3) concentration of metal is taken into account, only three metals (Cd, Co, and Ni) exceeded the safe HQ level. Therefore, these metals may result in non-carcinogenic health effects to the exposed population, posing a risk to human health. In addition to this, total HQ value for CP and FP was found to be 7.5 and 14.3 for total metal content which was decreased to 4.1 and 7.6 for easily accessible portion, respectively. The higher HQ value for FP as compared to the CP signifies the greater risk associated with the inhalation of fine particles for the residents of this area.

International Agency for Research on Cancer (IARC) has recently designated particulate matter in ambient air as a Group 1 carcinogen (Hamra et al. 2014). In 2010, 223,000 deaths occurred worldwide due to lung cancer linked with air pollution (Barret

Table 3 Individual contamination factor (ICF) and global contamination factor (GCF) of metals in coarse and fine PM

Contamination type	Coarse	Fine
ICF < 1 (low contamination)	Cu (0.9) Fe (0.8) Ni (0.9) Zn (0.6)	Fe (0.6)
1 < ICF < 3 (moderate contamination)	Mn (1.6)	Zn (2.6) Fe (1.2) Mn (1.5) Ni (1.8)
3 < ICF < 6 (considerable contamination)	Pb (4.9) Co (3.0) Cr (5.2)	Cu (3.1) Cd (4.7) Co (5.5) Cr (3.7)
ICF > 6 (high contamination)	Cd (7.6)	Pb (7.4)
Global contamination factor (GCF)	27.0	34.3

Table 4 Average non-cancer and cancer risk assessment for coarse and fine PM

(a) Non-cancerous risk assessment in terms of hazard quotient

Rfc/Rfd		Fine			Coarse		
		F1 + F2	F1 + F2 + F3	TMC	F1 + F2	F1 + F2 + F3	TMC
Cu[b]	4.0×10^{-2}(mg/Kg/day)	3.0×10^{-4}	7.9×10^{-4}	1.1×10^{-3}	9×10^{-5}	4.4×10^{-4}	9.5×10^{-4}
Zn[b]	3.0×10^{-1}(mg/Kg/day)	1.0×10^{-4}	2.0×10^{-4}	3.0×10^{-4}	1.0×10^{-4}	1.0×10^{-4}	2.0×10^{-4}
Fe[b]	3.0×10^{-1}(mg/Kg/day)	1.0×10^{-4}	5.0×10^{-4}	1.4×10^{-4}	4.0×10^{-4}	1.4×10^{-3}	3.1×10^{-3}
Pb[b]	6.0×10^{-3}(mg/Kg/day)	4.8×10^{-3}	6.0×10^{-3}	8.8×10^{-3}	2.7×10^{-3}	3.4×10^{-3}	4.5×10^{-3}
Cd[a]	1.0×10^{-5} (mg m^{-3})	1.1	1.4	1.8	1.3	1.4	1.6
Mn[a]	5.0×10^{-5}(mg/m^3)	3.1×10^{-1}	5.0×10^{-1}	8.3×10^{-1}	3.9×10^{-1}	7.8×10^{-3}	1.5
Co[a]	6.0×10^{-6}(mg/m^3)	1.6	2.1	2.8	5.5×10^{-1}	1.7	2.4
Cr[a]	1.0×10^{-4}(mg/m^3)	2.2×10^{-1}	4.2×10^{-1}	5.9×10^{-1}	2.4×10^{-1}	3.6×10^{-1}	4.4×10^{-1}
Ni[a]	1.4×10^{-5}(mg/m^3)	1	3.1	8.3	3.1×10^{-1}	6.7×10^{-1}	1.6
Total HQ		4.2	7.6	14.3	2.8	4.1	7.5

(b) Cancer risk assessment

	Unit risk[a] (μg/m^3)$^{-1}$	Fine			Coarse		
		F1 + F2	F1 + F2 + F3	TMC	F1 + F2	F1 + F2 + F3	TMC
Pb	0.000012	0.5E−06	1.5E−06	2.1E−06	0.1E−06	0.8E−06	1.8E−06
Cd	0.0018	80E−06	110E−06	130E−06	75E−06	98E−06	120E−06
Cr	0.012	142E−06	285E−06	400E−06	157E−04	242E−06	300E−06
Ni	0.00048	27E−06	84E−06	220E−06	8.4E−06	18E−06	43E−06

TMC total metal concentration

[a] Rfc = Reference concentration for metals, viz,. Cr, Ni, Mn, Co, and Cd (USEPA 2013)

[b] Rfd = Reference dose for metals, viz., Cu, Zn, Fe, and Pb (USEPA 2013)

2014). Out of the 10 studied metals, only four (Pb, Cd, Cr, and Ni) are found to be human carcinogens. The unit risk of two known carcinogens (Cr and Ni) and one probable carcinogen (Cd) was obtained from US EPA Integrated Risk information system (IRIS). In case of Cr, carcinogenic risk assessment was calculated for Cr (VI) (human carcinogen). It was calculated as one-seventh of the total concentration as the ratio of carcinogenic Cr(VI) to non-carcinogenic Cr(III) in ambient air is about 1:6 (Khanna et al. 2015). The unit risk for Pb, group B2 probable carcinogen, was obtained from a study by Greene and Morris (2006). The average value of unit risk calculated for CP and FP is presented in Table 4. Any cancer risk less than 1×10^{-6} is considered negligible by US EPA. Using both TMC and easily accessible metal concentration, the cancer risk estimated for Cd, Ni, and Cr in both CP and FP is much higher than the acceptable limits of US EPA. The estimated risk for TMC was 0.8–2.6 times higher than the risk calculated by using the easily accessible metal concentration. The highest cancer risk was found for Cr followed by Cd. This may be due to the higher unit risk value for Cr and high contamination level of Cd in the samples. The cancer risk was higher for FP as compared to CP fraction.

Conclusions

The results from the study reveal that the average mass concentration of $PM_{2.5}$ and PM_{10} collected during the sampling period was higher than the Indian National Ambient Air Quality Standards and WHO standards. Seasonally, the concentrations of both the particle sizes were found to be higher in winter season than in summer and monsoon. The results of sequential extraction procedure indicated higher percentage of

Pb, Cd, and Cr accumulated in the mobile fraction (F1 + F2), whereas higher percentage of Ni, Fe, Mn, and Cu was found predominantly in residual fraction. Zn and Co were equally distributed in the mobile and bound to oxides and carbonates fraction. Fe is found to be the dominant metal followed by Zn in both coarse and fine samples. PCA revealed that the airborne particles collected in Pune city during the sampling period are strongly impacted by anthropogenic sources. The sources like vehicular activity, coal combustion, industrial emissions, electronic waste dumping, construction activities, waste incineration, soil and road dust are possible key contributors to the PM-bound metals. The results of the health risk assessment showed that total metal concentration of Co, Ni, Mn, and Cd exceeded the respective HQ, while HQ value of Mn was found to be with safe HQ when easily accessible concentration was considered. The total as well as easily accessible concentration of Cr, Ni, and Cd exceeded the carcinogenic unit risk for the residents of Pune city. This study indicated that air particle pollution may possess serious health risks to the residents of this city. The results of this study represent a baseline study for evaluating the air quality status of Pune in terms of PM and the associated health risk. A more thorough study is required not only in terms of temporal and spatial parameters, but also a more complete chemical analysis of the particles components, which in addition to heavy metals, will include the organic components associated with PM.

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