Chapter 2
Quantification of Airborne Particulate and Associated Toxic Heavy Metals in Urban Indoor Environment and Allied Health Effects

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Abstract The present chapter is an attempt to summarize the importance of indoor air quality, which can be considered as IAQ and to emphasize on the hazardous effects of particulate matter (PM) consisting of fine and ultrafine particles. Indoor air pollution is a leading cause of poor health outcome in India. Nano particles in indoor air have been linked to growing cardiovascular diseases and premature deaths in India. Metals are associated with particulate matter. Heavy metals are produced by non-exhaust discharges, fuel additives and by extraction processes. They are considered to be hazardous mainly because of their potential to produce reactive oxygen species in respiratory system. The purpose of this chapter is explained by a case study undertaken in Lucknow city where particulate matter ($PM_{2.5}$, PM_{10}) and associated heavy metals viz. Fe, Zn, Pb, Cr, Ni, Cu and Mn were analyzed in three microenvironments namely (1) well planned, (2) densely populated and (3) roadside, over a period of two years (2012–2014). Identification of the main sources of the heavy metals was done through principal component analysis. Calculation of enrichment factors was also done for heavy metals to know their source of origin. Human health is generally affected by the accumulation of pollutants in the body. Even though the hazardous effects of heavy metals are known, still there is limited knowledge on association of a disease with inhalation exposure, particularly in indoor environment. The issue needs more focus to understand the causes, harm and to recommend actions to check the emissions and lower the ill effects.

Keywords Indoor air · Metals · Particulate matter · Urban emissions

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2.1 Introduction—Indoor Air Quality and Its Importance

India, as a developing country is witnessing poor outdoor as well as indoor air quality. Indoor air pollution (Census of India 2011) contributes to approximately 2.6% of the global burden of disease and 1.6 million pre-mature deaths annually (Smith and Mehta 2003; Balakrishnan et al. 2011). World Health Organization (WHO) has designated the problem of indoor air pollution (IAP) in top five perilous global environmental issues in progressing nations (World Health Organization 2002). The report on Global Burden of Disease (GBD) has reported 2 million early deaths yearly in India owing to IAP (Global Burden of Disease 2016). Though, indoor usage of biomass burning is accountable for less than one-fourth of the mass of particulate matter suspended in ambient air, suggesting importance of other sources which are responsible for particulate emission. Hence country specific solutions are needed to tackle the emission (Chafe et al. 2014). Indoor air quality (IAQ) is dependent on the level of ambient air pollution to an appreciable extent, owing to infiltration and penetration. Household sources also significantly contribute to outdoor environment, hence making them inter-dependent. Thus the two phenomena cannot be accurately studied in isolation or considered as separate entities (Balakrishnan et al. 2014). Air pollution exposure whether occurred outdoor or indoor has a common impact on health. The risk of exposure is equal for both rural and urban populations, though the sources contributing to the pollution may be different in both environments. However due to partial significance to urban centres, the overall understanding of the nature and distribution of pollutants is somewhat lacking (Garaga et al. 2018). Another important aspect of consideration is exposure to local sources like use of biomass, garbage burning, emerging small scale industries which contribute significantly to large spatial gradients that cannot be accounted for, while monitoring at the specific or central sites (Pant et al. 2016). For instance, metropolitan cities usually have high ambient levels of particulate contamination, whereas in rural settings, higher values of the same can be obtained in households, due to biomass exposure, hence exposure-response relations will be unlike, for different settings and should be tackled separately in urban and rural populations. Other than criteria pollutants many hazardous pollutants like toxic heavy metals, poly aromatic hydrocarbons (PAHs) can be associated with particulate matter, which are usually prevalent in urban industrial areas. They are released along with other particulate species and lead to severe health outcomes (Guo et al. 2017). A comprehensive air pollution assessment study would include all factors of significance including emission inventory, exposure pathway, exposure to population, toxicity factors and health outcomes (Gordona et al. 2018). The objectives of the present investigations were to carry a distribution of heavy metals including Fe, Pb, Mn, Cu, Ni, Cr and Zn in the indoor environment of urban Lucknow homes, in two size ranges of particulate viz. $PM_{2.5}$ and PM_{10} and to elucidate the relationship between the levels of metals in these sizes. The results have practical importance in identifying sources and processes that control levels of fine particulate matter.

2.1.1 Monitoring of Indoor Air Pollution

Slight modifications may be made in the tools and instruments used for ambient pollution monitoring, making them adaptable for indoor pollution monitoring. Personalized monitors are constantly used for the determination of individual exposure to air pollutants. The indoor environment has a limited air volume and comparatively lesser rate of air exchange. Hence while drawing an indoor sample, it is important to adjust the sampling flow at a slower rate so that the indoor air movement and air exchange rates are not affected. Instruments can measure pollutants directly, or they may be absorbed for further laboratory analysis (https://www.ncbi.nlm.nih.gov/books/NBK234059/; U.S. Environmental Protection Agency 1980). Air sampling techniques have been categorized as follows:

Continuous Monitoring
Continuous monitoring is needed to measure both temporal and spatial concentrations variation which is essential for indoor air pollution modeling. The continuous sampling also gives an insight to occupant's exposure and the levels of variability. The key advantage of continuous monitoring is the determination of short-term varying concentrations. The average concentration of pollutant measured over a period of time may depend on the factors such as infiltration, ventilation and source generation. Continuous monitors do require regular calibrations. They are also costly and need high maintenance. Safety hazards are also associated with them and they work at a set power level. They can also produce noise and heat, thereby creating hindrance in daily measurements (Moschandreas et al. 1978). Continuous monitoring is not suitable for large-scale surveys, owing to time and cost limitations.

Integrated Sampling
In this method an average data is obtained over a specific period of time. Integrated sampling is used when the mean concentration is either necessary or acceptable. The time period can vary from minutes to weeks or months. Analysis can be done at the sampling site, which may be indoor or outdoor. The results are presented as average concentration for the sampling period. A variety of pollutants are monitored by integrated sampling. Particulate matter can be sampled on a filter paper which can be subjected to gravimetric or chemical analysis. Size-specific samplers are also used for indoor sampling which can collect particulate matter of less than 2.5 μm diameter (Loo et al. 1979) or particles smaller than 3.5 μm in size. The particle samplers range from handy units which are manually operated to completely automated devices that are programmed to work automatically without manual handling. Gaseous pollutants can be measured by both passive (diffusion-controlled) and active (powered bulk airflow) samplers. Integration sampling is cost effective and requires less manpower. Pollutants in very low concentrations can also be measured by adopting a suitable sampling/measurement technique. On the contrary, there is loss of short-term temporal information. Frequent sampling must be done if temporal variability is to be studied (Schuette 1967).

2.2 Criteria Pollutants and Their Effects

Environmental Protection Agency (EPA) has established national ambient air quality standards (NAAQS) for six pollutants known as criteria pollutants viz. carbon monoxide, lead, ground-level ozone, particulate matter, nitrogen dioxide and sulfur dioxide. They can be emitted in air by various sources. The standard limits are set to check their emission and to protect public health. The main sources and effects associated with the six criteria pollutants are given in Table 2.1.

2.2.1 Particulate Contamination—A Death Trap

Particulate matter (PM) can be derived from an array of heterogeneous sources differing in chemical composition and physical state and is differentiated or classified by it's size (Ingrid et al. 2014) as given below:

- PM_{10}- less than 10 µm (10 microns) in diameter
- $PM_{2.5}$- less than 2.5 µm in diameter,
- $PM_{1.0}$- less than 1 µm in diameter.

Particles ranging between 2.5 and 10 µm in diameter are known as coarse particles. Particles less than 2.5 µm in diameter are fine particles including ultrafine (less than 0.1 µm) ($PM_{0.1}$).

Primary particulate matter: is released into the atmosphere by a number of anthropogenic and natural sources.

Secondary particulate matter: is formed by physical and chemical reactions via other pollutants.

Re-suspended particulate matter: after its deposition, particulate matter can be re-suspended into the air through the movement of wind or through vehicular exhaust (Tolis et al. 2014).

Particles with large size can be removed by mechanical methods, like cyclone and gravity collectors etc. whereas electro-filters are used to remove finer particles. It has been found that the productivity of an electro-filter relies upon the resistivity of the particles, which depends upon their chemistry (Zhang et al. 2018; Qin and Wang 2006) and can also serve as a carrier of harmful elements such as As, Be, Cd, Pb, Mn and Ni (Hu et al. 2012).

2.2.2 Generation of Particulate Matter

Particulate matter is generated from the following sources:

1. **Mechanical sources**: Through metallurgical operations like powdering, crushing, cracking etc.

Table 2.1 Emission and effects of criteria pollutants

Criteria pollutant	Emitting source	Health effect	Environmental effect
Sulfur dioxide (SO_2)	Volcanic emissions, fuel combustion, metal smelting, industries (http://cfpub.epa.gov/ncea/isa/recordisplay.cfm?deid=1988)	Breathing difficulties, Respiratory Problems including wheezing, chest tightness, or shortness of breath, heart and lung disorders, visual impairment (http://cfpub.epa.gov/ncea/isa/recordisplay.cfm?deid=1988)	Acid rain
Nitrogen dioxide (NO_2)	Fossil Fuel burning, biomass, high temperature combustion (ENVIS Centre on Control of Pollution 2016) processes power plants, non-road engines and equipment	Respiratory symptoms, Pulmonary disorders	Precursor of ozone formation in troposphere (ENVIS Centre on Control of Pollution 2016)
Particulate Matter (PM)	Vehicular exhaust, Industrial commercial and residential (ENVIS Centre on Control of Pollution 2016) combustion, construction activities	Respiratory problems, exacerbation of allergic symptoms (ENVIS Centre on Control of Pollution 2016), liver fibrosis, lung/liver cancer, heart stroke, premature mortality	Reduced visibility
Carbon monoxide (CO)	Gasoline-fueled vehicles, Combustion of carbonaceus fuels, emission from IC engines (http://www.epa.gov/air/caa/)	Reduced oxygen carrying capacity, anorexia, cardiovascular problems, myocardial ischemia (http://www.epa.gov/air/caa/)	Climate change and green- house effect

(continued)

Table 2.1 (continued)

Criteria pollutant	Emitting source	Health effect	Environmental effect
Ozone (O_3)	Hydrocarbons and NO_X react with sunlight to produce O_3, pollutants emitted by industrial facilities, electric utilities, and vehicles, substances generating ozone can also be emitted by anthropogenic sources, especially plants (http://cfpub.epa.gov/ncea/isa/recordisplay.cfm?deid=1499)	Respiratory problems, asthma, bronchitis etc. inflammation of lung and symptoms such as cough, wheezing, chest pain and shortness of breath etc. (Saadeh and Klaunig 2015)	O_3 in upper troposphere produces greenhouse effect, hazardous effects on plants in the form of interference in photosynthesis (ENVIS Centre on Control of Pollution 2016)
Lead (Pb)	Metallurgical operations, vehicular exhausts, lead-acid batteries, industrial wastes etc. (ENVIS Centre on Control of Pollution 2016)	Central nervous system disorders in children, anemia, toxic for soft tissues and bones (http://cfpub.epa.gov/ncea/isa/recordisplay.cfm?deid=1588)	Disturbed soil functioning

2. **Chemical or thermal sources**: These sources generate particulate matter through chemical or high-temperature evaporation reactions followed by the condensation.
3. **Biological sources**: Include pollen grains, fungi and bacteria.

Generation of particulates human activities: Generation of particulate matter takes place usually through the following activities:

1. Ploughing
2. Construction activities
3. Mining
4. Combustion of solid fuels, liquid fuels and biomass
5. Vehicular exhaust

Particulate emission from the natural sources is usually associated with volcanic eruptions, forest fires and soil erosion etc. (Pio et al. 2008; Oucher et al. 2015). According to WHO air quality guidelines, a reduction in yearly average $PM_{2.5}$ concentrations up to 10 μg/m^3 could lead to reduced air pollution related deaths by 15% in developing countries (WHO 2018). The low and middle income group countries have faced a lot of exposure to particulate matter usually originating from the household combustion of inferior fuel in traditional inefficient stoves, thereby increasing the risk for respiratory and cardiovascular diseases including acute lower respiratory infections, chronic obstructive pulmonary disease (COPD) and lung cancer (WHO 2018). An estimation done by WHO's International Agency for Research on Cancer (IARC) in 2013 revealed that particulate matter is the vital factor for increased vulnerability for cancer, especially pertaining to lungs. A relationship has been established between ambient pollution and risk of urinary tract/bladder cancer (WHO 2018). The particulate matter has bad effect on human health as well as on environment in the form of reduced visibility which results due to absorption and scattering of sunlight. In India, if the particulate level remains at its current status, per-capita mortality rate would increase by 21% by the year 2030. The average particulate emission should be reduced by 20–30% in the coming fifteen years to reduce the mortality rates. A large number of epidemiologic studies have demonstrated a correlation between enhanced ambient particulate levels and hospital admissions for respiratory diseases (Fusco et al. 2001; Spix et al. 1998; Atkinson et al. 2001; Migliaretti et al. 2005; Sun et al. 2006) (Table 2.2).

By following the air quality guidelines a gradual shift can be made in the concentrations at present. Hence it should be the major objective to follow the guidelines

Particulate matter	Annual mean (μg/m^3)	24-hour mean (μg/m^3)
Fine particulate matter ($PM_{2.5}$)	10	25
Coarse particulate matter (PM_{10})	20	50

Table 2.2 WHO 2005 guidelines for ambient particulate matter (Ambient (outdoor) air quality and health WHO, 2nd May 2018)

compulsorily. The risk exposure to the particulate matter is same for the people residing in urban and rural areas, although people in growing cities are at higher risk than those in developed ones.

2.2.3 Indoor Particulate Concentration and Health Impact

Not only that the outdoor particulate matter can infiltrate indoors, but it can also be generated by indoor sources as well. There is a growing interest to study about the specific impacts of indoor PM on human health.

Health Effects of Inhalable Particles
Respiratory and cardiovascular systems are affected largely due to the exposure to particulate matter. Studies have suggested association between health problems and size of the inhalable particles. Particles having small size viz. less than 10 μm in diameter have a tendency to penetrate deep into the lungs even reaching to the bloodstream. Those with heart or lung diseases are more vulnerable to get affected from PM exposure. Children and older adults are the most susceptible groups to be affected. Researches have linked PM exposure to a variety of health impacts, including:

1. Eye, nose and throat irritation.
2. Aggravation of coronary and respiratory disease symptoms.
3. Premature death in people with heart or lung disease.

2.2.4 Fine and Ultrafine Particles

Particulate matter is mostly sub-classified in two main classes groups: coarse and fine particles. Generally particulate matter is defined as either $PM_{2.5}$ (size less than 2.5 μm) or PM_{10} (size less than 10 μm). Though limits have been defined to control $PM_{2.5}$ and PM_{10}, there are no such limits or standards for ultrafine particles, as PM_1 (less than 0.1 μm or 100 nm to 1 μm) and $PM_{0.1}$. The defense mechanism of human respiratory system does not work against ultrafine particles (UFPs). WHO has not defined threshold limit for ultrafine particles like PM_1, which is seventy times finer than a human hair. Fine and ultrafine particulate matter (PM_1) is found in the form of a complex mixture in ambient atmospheric aerosol (Mauderly and Chow 2008).The particles ranging in size below <0.1 μm are known as the ultrafine particles (Hinds 1999). Because of their large surface area and high number density, they have high pulmonary deposition efficiency. Ultrafine particles are important in atmospheric chemistry research, particularly because of the associated health factors. They also carry substantial quantities of adsorbed or condensed toxic air pollutants including organic compounds and transition metals (Oberdörster et al. 2002). Vehicular load is

identified as the key reason of ultrafine particulate emission (Shi et al. 2001; Keogh et al. 2009) contributing to around 60% particle number concentration (PNC) and 90% along the roadside in cities with high pollution level. People residing near main roads have a high exposure rate to ultrafine particulate matter and have shown escalation in the incidences of severe health issues, because of heavy traffic flow (Kumar et al. 2014; Pey et al. 2009; Pérez et al. 2010). Owing to their fine size these ultrafine particles can establish contact with the body through skin. Studies have linked skin diseases with prolonged exposure to ultrafine particles among the industry labors. PM_1 is efficient to penetrate through the cardiovascular system, prompting heart diseases. Cardiovascular mortality has also been associated with the inhalation of ultrafine particles. PM_1 has also been associated with premature births and abnormal foetal development. There has been limited research in developing countries like India to assess the health impact and severity of ultrafine particles in environment (Jayanthi et al. 2012; Verma et al. 2014; Bhardawaj et al. 2016). India's present vehicle count is around forty million, with an increase of 5% per annum, thus exposing its population to hazards of UFPs (Kumar et al. 2012).

### 2.2.5 Mechanism of Formation of Ultrafine Particles

They may be released in the environment by at these processes:

(a) **Direct emission**—Through vehicular or industrial sources (Kumar et al. 2012).
(b) **Combustion**—Combustion may also emit hot supersaturated vapors, which undergo nucleation and condensation while getting cooled to normal temperatures.
(c) **Chemical reactions**—Chemical reactions in the atmosphere may lead to the formation of UFPs that are more "localized," with their concentrations diminishing with distance to their sources.

Sources of Ultrafine Particles
Vehicular exhaust—The main source of atmospheric ultrafine particles is automobile exhaust (Pennington and Johnston 2012). In conjugation with roadside atmosphere, UFPs may result in the formation of condensable organic compounds (COCs) (Minoura et al. 2009). Increasing pollution episodes and closeness to high-traffic roads significantly contribute to the concentration of UFPs (Gramotnev and Ristovski 2004; Oberdörster et al. 2005). Particles generated from diesel driven vehicular exhaust are between 20 and 130 nm in size (Morawska et al. 1998) and 20–60 nm for gasoline engines (Ristovski et al. 1998). Highest concentrations are usually reported during morning when people are leaving for work and children are going to school (Imhof et al. 2005; Jain et al. 2011).

   Photochemical reactions—UFPs can also result by photochemical reactions at ambient temperature. Low-volatility species are formed due to these reactions which lead to the formation of UFPs by nucleation (Kulmala et al. 2004) which may occur
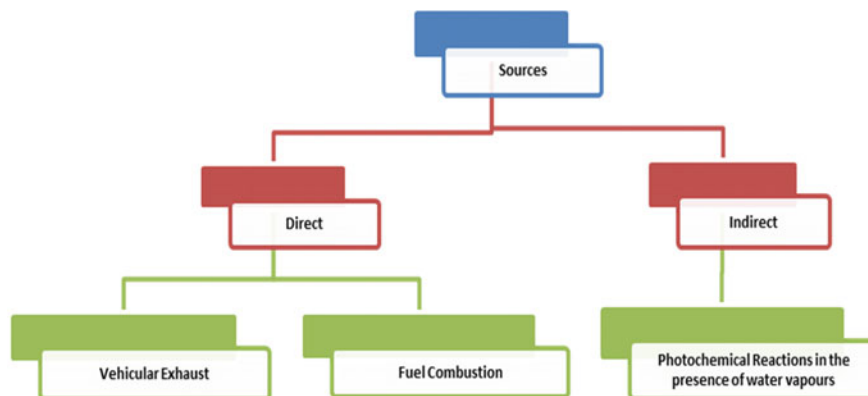
Fig. 2.1 Sources of ultrafine particles

on ions and possibly is a multicomponent process. Evidences suggest that sulphuric acid vapors help in nucleation. Binary water-sulphuric acid mechanism has been proposed for nucleation (Kulmala and Laaksonen 1990). Ternary water-sulphuric acid-ammonia nucleation has also been suggested (Yu and Turco 2000). The small sized particles can condense through low-volatility organic species condensation which is produced through photochemical oxidation of low volatility organic species (Kulmala et al. 2004).

Biofuel usage—Biofuels have been used as an alternative to overcome pollution from conventional fuels (Bhardawaj et al. 2016). Though biofuels produce reduced particle mass but consist of higher PNC including ultrafine particles (Bhardawaj et al. 2013). Biofuels with low calorific values are required in higher volumes with an amplified fuel flow rate. Hence biofuels must be introspected and appropriate mitigation strategies should be evolved, which diminish UFP production from them and minimize health risks (Lapuerta et al. 2008) (Figs. 2.1 and 2.2).

2.2.6   *Health Effects of Ultrafine Particulates*

Ultrafine particulate matter can enter the human body through inhalation, dermal, oral, olfactory or through digestive routes. They deposit in the respiratory tract and travel to other organs. They penetrate into lungs causing acute and chronic illnesses including asthma, COPD and childhood leukemia etc. (Ezz et al. 2015; Qiao et al. 2015; Ajmani et al. 2016; Peters et al. 1997). A negative correlation has been established between ultrafine particles and peak expiratory flow (Penttinen et al. 2001), whereas a positive correlation between cardiovascular mortality and fine and ultra-fine particles has been established in two pollutant models (Wichmann et al. 2000; Oberdörster et al. 2002). The biological response of UFPs is dependent on its minis-cule size and high surface area where damaging organic chemicals can be adsorbed

DIRECT RELEASE OF PARTICLES
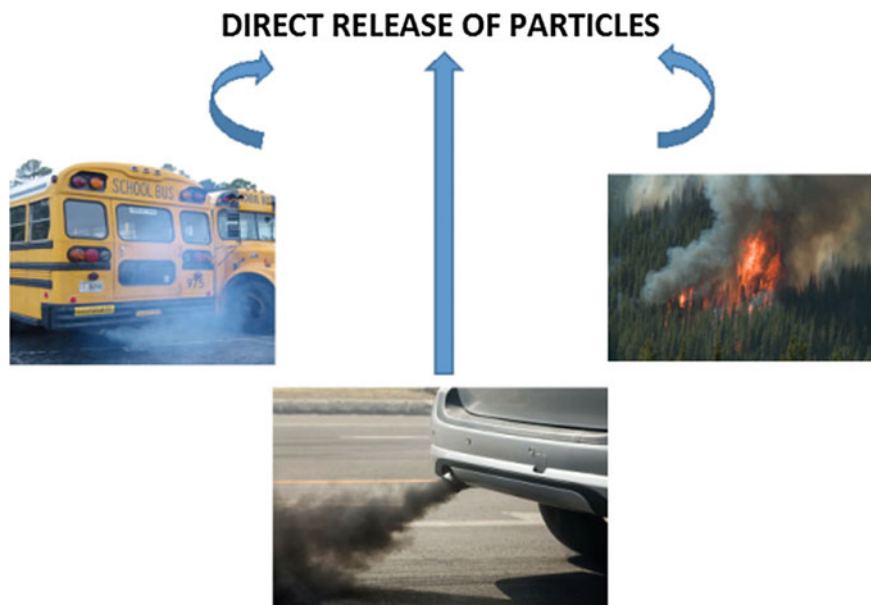
Fig. 2.2 Release of particles in environment

(Block and Calderón-Garcidueñas 2009) which are further moved to the pulmonary system and are finally mixed into blood stream which can affect heart and central nervous system through inflammation (Genc et al. 2012).

2.2.7 Indoor Particulate Sources

Indoor particulate matter can be originated both from outdoor as well as indoor sources. Common indoor particulate matter originates from cooking and combustion activities like, use of unvented heaters or stoves, fireplaces and use of inferior quality fuel for various household purposes. Cigarette smoking is another factor that contributes to the indoor particulate matter. Biological sources may also contribute significantly in the production of particulate matter (Pekkanen et al. 1997; Adams et al. 2015). In India, the studies have mostly concentrated on indoor air pollution due to combustion of biomass fuels in inefficient cooking stoves in rural and semi urban areas. In these microenvironments indoor air quality has been linked with their socio-economic status which makes it difficult for the rural population to afford environment friendly fuel (Awasthi et al. 1996; Balakrishnan et al. 2002; Bruce et al. 2000; Kulshreshtha et al. 2008; Singh and Jamal 2012). Exposure to household generated smoke is more severe in developing countries as large proportions of households are

still dependent on biofuels for cooking and other household purposes. Poor ventilation in such households exacerbates the situation producing large volumes of smoke indoors (Bruce et al. 2000). Women are more prone to the exposure of particulate contamination because they are mostly involved in cooking (Behera et al. 1988) and young children who tend to stay indoors (Albalak et al. 1999). Indoor particulate quantification is important for the assessment of the total human exposure to pollutants (Varghese et al. 2005). Many studies have assessed exposure of particulate matter generated from cooking in many Indian areas (Kulkarni and Patil 1999; Saksena et al. 2002) including the potential health risks in different microenvironments. Health effects of particulate matter depend upon several factors including physiological, physical, chemical and biological (Dreher 2000). Though previous studies have established a strong relationship between the biofuel usage and production of particulate matter, especially in rural households, still there is no concrete evidence which reveals the generation and size distribution of the particulate matter generated in urban areas of India where energy resources are different. Less data is available which highlights the problem of indoor air pollution in urban areas as the studies have been more focused on the ambient pollution. To predict indoor air quality, we have to take an account of a variety of indoor sources, other than biomass fuel burning (Goyal et al. 2012). Some of the chief elements affecting the IAQ are: (i) concentrations of ambient pollutants infiltrating indoors (ii) building constituents such as asbestos, cement etc. (iii) indoor characteristics such as ventilation, (iv) occupancy inside a dwelling (v) equipments used indoors (vi) rituals, habits and practices of the occupants, and (vii) the financial standing of the dwellers (Kumar 2011).

2.3 Particulate Matter and Associated Heavy Metals

Heavy metals are mostly associated with particulate matter and get absorbed in human body via inhalation. These heavy metals have severe physiological effects. Strong evidences have suggested that heavy metal adsorption is crucial to the adverse effects associated with particulate matter (Bollati et al. 2010). Heavy metals are metallic elements with high density, specific gravity and atomic weights (Duffus 2002). They enter the environment mainly through deposition of atmospheric particulates; disposal of metal containing sewage, traffic emission, re-suspension of road dust and through mining operations (Shrivastav 2001). Re-suspension of roadside dust is a chief source of heavy metals (Schroeder et al. 1987). Mn, Cu, Zn, Cd, Cr, Fe, Ni, K, Ca, V, Ba, As, Se and Sr are some of the metals which have been commonly studied. Ultrafine particulate emitted from diesel exhaust is considered to be very toxic due to its high metal content which causes oxidative stress leading to endothelial dysfunction and increased risk of heart dysfunction (Miller et al. 2012). $PM_{2.5}$ is considered more dangerous because of its longer retention time and deeper penetration in lungs (WHO 2006). A person is more susceptible to the exposure of particulate matter indoors because people spend 90% of their time indoors (Massey et al. 2013). Influence of the inhaled aerosols depend on the chemical species, its concentration, extent

of exposure in terms of time and its deposition within the respiratory tract (Salma et al. 2002). Fine particles have a higher tendency to absorb toxic metals than coarse particles (Massey et al. 2013). Outdoor particulate matter can reach indoors and affect the indoor concentration potentially. Ventilation has also been found to effect the indoor PM concentration, which is also dependent on the source characteristics and physical nature of pollutants (Leung 2015). Heavy metals exert toxic effects (Erisman et al. 1994) hence their assessment is of enormous importance for toxicological, environmental and occupational studies concentrating on health outcomes (Pandey et al. 1998).

2.3.1 Hazardous Effects of Heavy Metal Borne Particulates

A number of adverse health consequences have been linked with heavy metal borne particulate contamination. Incidences of myocardial infarction have been linked with particulate contamination. Ultrafine particles induce oxidative stress in the endothelium, and reach other structures through the nervous system. Thrombosis, heart rate fluctuations and blood pressure changes have been related with particulate matter (Anderson et al. 2012) and lately irregularities in glucose metabolism have been reported. Low birth-weight, infertility, genotoxicity and cancer (Loomis et al. 2014) are also associated with PM exposure. Some of the health effects associated with heavy metals carried by inhaled particles have been summarized in Table 2.3.

2.3.2 Mechanism of Action of Heavy Metals

The exact mechanism through which heavy metals exert hazardous effects is not known, still it has been found that metals cause oxidative stress, inflammation and changes in the immune response (Wiseman and Zereini 2009). Cr, Cd and Ni have been found to alter the DNA's repairing ability which is an outcome of oxidative stress. Alterations in the microstructure of the non-ciliated bronchilar cells have also been reported after Pb inhalation (Fortoul et al. 1999). Cardiovascular effects of the metals have been found to occur through inflammation and the initiation of hypercoagulability and endothelial dysfunction (Martinelli et al. 2013). High concentration of Ni, Cu and As has been linked with high level of C-receptor protein, interleukin-6 and vascular endothelial growth factor showing low capacity of endothelial repair (Niu et al. 2013). Cd carcinogenicity has been associated with the generation of ROS owing to the inactivation of detoxifying enzymes like catalase, glutathione peroxidase etc. Cu has been identified as the rate-limiting nutrient for tumors. The presence of Cu in tumors affects cytochrome c oxidase activity (Ishida et al. 2013). Mercury compounds have been found to inhibit mitotic spindle and alter DNA repair process. Hg has also been seen to deplete the immune system and could decrease immune tumor

Table 2.3 Health symptoms of common metals

S. No.	Metal	Source	Health Symptoms (short and long term)
1	Pb	Anti-knocking agent in gasoline	1. Changes in bronchiolar cells (Soto-Jimenez and Flegal 2011) 2. Increased cancer risk 3. Alterations in DNA synthesis, mutations (Silbergeld 2003) 4. Cell proliferation and oxidative stress (Garcia-Leston et al. 2010)
2	Ni	Refineries, industries, cigarette smoke	1. Cancer risk 2. Chromosome aberration in rats (Chorvatovicova and Kovacikova 1992) 3. Cardiovascular diseases
3	Cd	Cigarette smoke	1. Genotoxicity (Fortoul et al. 2015) 2. Disruption of cell adhesion causing tumour progression (Koedrith and Seo 2011) 3. Liver damage through ROS generation (Fowler 2009) 4. Elongation of estrous cycle in rats 5. Affects the synthesis of placental hormones like progesterone (Caserta et al. 2013) 6. Oxidative stress
4	Fe	Steel manufacturing industries, cement mills	1. Alterations in immune functions (Nairz et al. 2014) 2. Overload results in insulin resistance, hyperglycemia, elevated risk of Diabetes Mellitus (Fernandez-Real et al. 2002; Ferrannini 2000) 3. Overload results in hypertension and increased cardiovascular risk (Jomova and Valko 2011)
5	Cr	Metallurgical processes- in the manufacturing of steel, spray painting, impurities in fuel additives, non-exhaust emission, cigarette smoke	1. Genotoxic 2. Alteration in DNA's repair capacity 3. Carcinogenic 4. Cause hypoglycemia (Mertz 1993) 5. Immunotoxic-causes inhibition of immunoglobin secretion (Mitra et al. 2012)

Table 2.3 (continued)

S. No.	Metal	Source	Health Symptoms (short and long term)
6	Hg	Forest fires, fossil fuels, hydroelectric, mining, pulp, and paper industries. Incineration of municipal and medical waste and emissions from coal-using power plants also contribute to mercury	1. Methyl mercury is a known carcinogen 2. Produces oxidative stress 3. Genotoxic 4. Lethargy, irritability, depression (Magos and Clarkson 2006) 5. Hyperglycemia (Chang et al. 2011) 6. Reproductive effects including abortion, stillbirth and menstrual disorders and reduced fertility (De Rosis et al. 1985)
7	Cu	Copper extraction, metal and electrical manufacturing, agricultural and domestic use of pesticides and fungicides, leather processing, and automotive brake pads	1. Formation of ROS (Theophanides and Anastassopoulou 2002) 2. Neurodegenerative diseases such as Parkinson (Modgil et al. 2014) 3. Wilson's disease- accumulation of copper in liver (Pietrangelo 1996)
8.	Mn	Gasoline additive methylcyclopentadienyl manganese tricarbonyl (MMT)	1. Neurotoxicity 2. Decrease in intellectual ability 3. Alteration of psychomotor development (Lin et al. 2012) 4. Tetragonic effect 5. Growth restrictor, embryonic death and bone alterations (Gerber et al. 2002)
9.	Zn	Industrial activities	1. Neurotoxin (Sorsa 2011) 2. Impaired glucose metabolism (Praveena et al. 2013) 3. Teratogen (Basu et al. 2014)
10	V	Burning of fossil fuel including petroleum, oil, tar and asphaltite etc.	1. Respiratory effects (Cakmak et al. 2014) 2. Carcinogenicity 3. DNA disruption (Galanis et al. 2009). 4. Initiation of hypoxia (Assem and Levy 2009) 5. Behavioral and cognitive disorders (Barceloux 1999)

response (Koedrith and Seo 2011). Cr(VI) induced carcinogenicity has been associated with free radical production and establishing the cancer phenotype (Hartwig 2013). Mn has been observed to interfere with DNA polymerases, mitochondrial function and activation of some cytokinases and MAPK cell signaling cascades in its cancer causing ability (Valko et al. 2005). The genotoxicity of heavy metals has been linked with chromosomal aberration and DNA damage (Sorsa 2011). Neurotoxicity of the metals has been credited to molecular level metal dishomeostatis and mitochondrial dysfunction. Metals like Mn have been found to cross the blood-brain barrier inducing tremors and production of other schizophrenic symptoms (Braidy et al. 2014). Metals have also been found to effect retina where phototransduction process takes place. In addition a gradual reduction in PL and enhancement of the oxidative stress biomarker-4-hydroxinonenal has been observed on exposure to V (Avila et al. 2013). Metals also exert hazardous effects on the reproductive system. Cd has been linked with the increase in the duration of estrous cycle in rats (Cervantes-Yépez et al. 2018; Baranski and Sitarek 1987). Cadmium accumulates in the placenta and effects the expression of metallothionein, which retains Cd, thereby preventing it from reaching the foetus. But overexpression of metallothionein stops Zn transportation to the placenta and decreases the placental permeability. (Caserta et al. 2013). High levels of iron during the human embryonic period may be teratogenic. Researches in mice have shown that an escalation of iron produces histological variations in the encephalon, as well as spine and ribs abnormalities (Weinberg 2010) (Fig. 2.3).
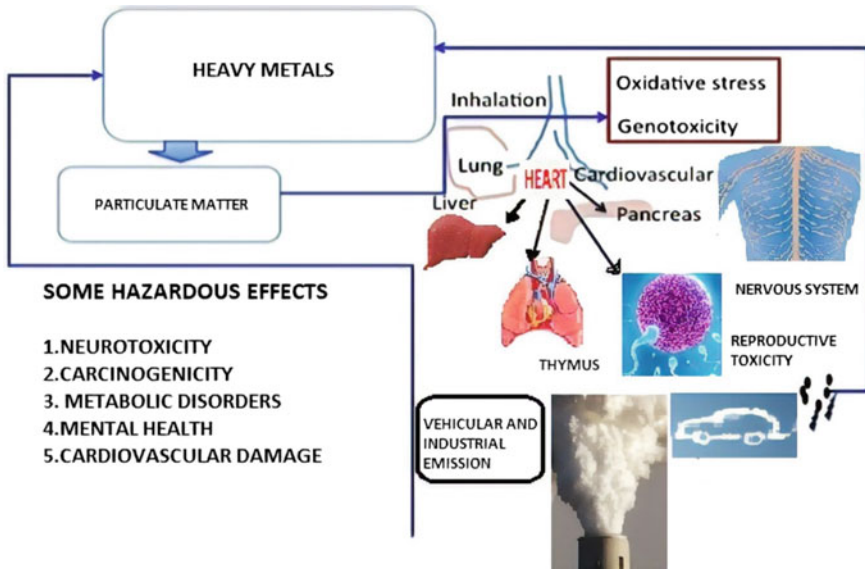

Fig. 2.3 Hazardous effects of heavy metals

2.4 Estimation and Analysis of Heavy Metals Associated with Particulate Matter—Parameters Employed

2.4.1 Source Apportionment

Source Apportionment (SA) is employed to identify sources of pollution and the quantification of their impact to pollution levels in ambient as well as indoor environment. The source apportionment can be done using different methods: emission inventories, source-oriented models and receptor-oriented models and is usually performed to assess the contributing sources to pollutant level at representative monitoring site. Among the variety of models being used to achieve source apportionment, receptor-oriented models are widely used as they have the benefit of providing information derived from online measurements. Receptor based models usually work to identify source contribution estimation at local and regional level all over the world. The outline for using receptor models to solve air quality problems consists of: formulating a conceptual model, finding potential sources, characterizing source emissions, sampling and analysis of ambient particulate matter samples, determination of source types using multivariate receptor models; quantifying source contributions with the chemical mass balance; assessing profile changes and reconciling receptor modeling results with source models, emissions inventories and eventually analysis of receptor data (Watson et al. 2002). The basic principle of receptor modeling is that mass conservation between the emission source and the study site can be anticipated, and a mass balance analysis can be done to recognize and apportion sources of pollutants. RMs recognize sources through the following mass balance equation

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \tag{2.1}$$

Where x_{ij} is the concentration of the j-th species in the i-th sample, g_{ik} is the contribution of k-th source to the i-th sample, f_{kj} is the concentration of the j-th species in the k-th source, and e_{ij} is the residual term. RMs are generally used to allocate PM concentration as categorized according to its chemical composition and heavy metals etc. From the analysis of particulate matter, it is enabled to assess the sources responsible for the total PM_{10} and $PM_{2.5}$ concentration accompanying several uncertainties (Karagulian et al. 2015).

2.4.2 Enrichment Factor Analysis

The enrichment factors (EF) of the elements are calculated to identify the source of the elements in the atmosphere. Other than that, the EF values can also define whether the elements have an additional contamination from the anthropogenic activities or

not. Aluminium (Al) and iron (Fe) are usually selected as reference elements for the crust based on previous studies (Enamorado-Báez et al. 2015). The equation for calculation of EF was proposed by Rahn (1976). The analysis is used to compare the concentrations of atmospheric aerosol elements, when they are present in higher concentrations. The EF can be calculated by the following formula

$$EF = \frac{[C]sample/[Cref]sample}{[C]crust/[Cref]crust} \qquad (2.2)$$

where

$[C]_{sample}$ = Concentration of C (analyte element)
$[C_{ref}]_{sample}$ = Concentration of the normalization reference element in the sample
$[C]_{crust}$ = Concentration in the continental rust
$[C_{ref}]_{crust}$ = Concentration in the continental crust for the reference element

Five categories have been defined on the basis of EFs: EF < 2, minimal enrichment; $2 \leq EF < 5$, moderate enrichment; $5 \leq EF < 20$, significant enrichment; $20 \leq EF < 40$, very high enrichment; and $EF \geq 40$, extremely high enrichment.

2.4.3   Chemical Mass Balance Modeling

The chemical mass balance (CMB) model is a popular receptor model for source apportionment. The model works on using solutions to linear equations attributing each receptor chemical concentration as a linear sum of products of source profile loads and source contributions. (Hidy and Venkataraman 1996). The CMB receptor method works on extracting information about a source's contribution on the basis of the profile variability of elements measured (Henry et al. 1984).

2.4.4   Principal Component Analysis (PCA)

Principal component Analysis is done to reduce the dimensionality of multivariate data without losing information. PCA analysis can be used to identify more clearly the various sources of particulate matter. Results can be plotted as different variables and interpretation can be done to obtain positive and negative correlations among them. The data set are subjected to Varimax rotation and Kaiser normalization for source apportionment. PCA data can be split up in specific groups which are known as factors and combine on the basis of similar features corresponding to similar originating sources and modes of transportation. The number of factors explains the highest maximum variance of the data (Vaio et al. 2018; Yang et al. 2016). To lessen the number of variables, Varimax rotation method is used to produce one rotated component matrix.

2.4.5 Instrumentation and Principle of Analysis of Heavy Metals in Particulate Matter

2.4.5.1 Flame-Atomic Absorption Spectroscopy

Atomic Absorption Spectrometry (AAS) is used for quantitative estimation of elements. The technique is based on measuring the absorbed radiation by the species under consideration. The atoms absorb ultraviolet or visible light and get promoted to higher energy levels. A detector is employed to measure the wavelength of light transmitted by the sample and makes a comparison with the originally passed light through the sample. The concentration is assessed by plotting a calibration curve, using standards of known concentration. The working principle of AAS depends on Beer-Lambert's law (Sammut et al. 2010). For precision, a light beam from a lamp whose cathode is made of the element being determined is passed through the flame. A photon multiplier detects the quantity of light intensity owing to absorption by the analyte, which is directly related to the concentration of the element in the sample (Welz and Sperling 1999).

2.5 Assessment of Heavy Metals Associated with Particulate Matter in Urban Environment—A Case Study in Lucknow Region

Lucknow is the capital of Uttar Pradesh, India. The city was earlier known as Awadh and is recognized for its rich cultural heritage, monuments and chicken work. The city is growing at a fast pace among all the nonmetropolitan cities. The city is a centre for industrial and real estate development depicting an economic boon. The growing urbanization has put the city under scanner as the level of air pollution has also shot up in the last few years (Verma et al. 2015). Lucknow City has a population of 2.82 millions as per 2011 census and emerging as one of the fastest growing cities. Deforestation is another major issue in the district which is leading to ecological imbalance. The actual forest cover in the district is about 115 km^2, which is less than 5% of the total area of the district (2500 km^2) as estimated in 2015. With the increase in vehicular load, roads need to be widened leading to felling of trees. The main causes of air pollution in Lucknow have been identified due to:

1. Vehicular exhaust and progressive increment in vehicular load.
2. Fast urbanization and loss of vegetation.
3. Nearby Industries.
4. Negligence of government and public.
5. Biomass combustion.
6. Open dumping and burning of the garbage (Saluja 2017).

2.5.1 Weather and Meteorological Factors

Lucknow has subtropical climate. Cool dry winter prevails from December to February and summers prevail from March to June. The maximum temperature in summer and winter is about 45 °C and 3 °C respectively. Annual rainfall is about 100 cm. Upon release in the ambient environment, a pollutant interacts with other pollutants and the concentration is influenced by micrometeorological factors which may affect its complexity making it more hazardous in nature. So it is necessary to identify the pollutants, their sources, transformation as well as fate of each pollutant and subsequently their impact on environment including living beings (Assessment of ambient Air Quality of Lucknow City 2017). Climate data retrieved from Lucknow Airport by Meteorological Department of India is shown in Table 2.4.

Foggy conditions prevail from late December to January. Summers are quite hot. The seasonal variability pattern of the pollutants shows a dynamic variation with gaseous pollutants being in high concentrations in winters and low concentration in monsoon. The difference in concentration level may be attributed to the wind speed. In winter season the comparatively highest concentrations may be attributed to low wind speed that is <5 km/h and high humidity. The stable atmospheric conditions hinder the vertical and horizontal instability for appropriate mixing of pollutants making them more stagnant in atmosphere. As a result, atmospheric dispersion is not adequate and pollutants accumulate near the ground breathing zone. The lack of precipitation during winters also decreases the capacity of wet deposition and related

Table 2.4 Meteorological data from Lucknow, India (http://www.imd.gov.in/section/climate/extreme/)

Month	Temperature (°C)			Rainfall (mm)
	Avg. high	Daily mean	Avg. low	
January	19	11.3	3.5	21
February	23.3	14.8	6.3	26
March	31.1	21.8	12.5	16
April	36.8	27.9	19	15
May	40	32	24	23.4
June	38.4	32.6	26.7	122.9
July	33.9	29.8	26	276.2
August	33.2	29	25.6	278.9
September	33.1	28.6	24.1	175.9
October	31	23.4	17.7	24.7
November	27.7	18.8	10	7.4
December	20.5	12.2	4.7	12.6
Yearly	30.7	21.7	16.7	1000

cleansing mechanisms. Washout effect is another factor playing an important role in monsoon which accounts for the low concentration of SO_2 and NO_2.

2.5.2 Air Pollution Status of Lucknow

During the recent years air quality in Lucknow has witnessed a down fall. Studies have correlated air pollution status with environmental, human and plant health impacts. The metallic concentration associated with particulate matter has been found to fluctuate with meteorological conditions in the region. A survey based study done in early 2000 showed that particulate concentration exceeded the NAAQS limits. Particulate fraction PM_{10} analyzed for heavy metals showed the presence of heavy metals in all the seasons (Pradhan et al. 2004). The study revealed significant variation in the metal concentrations at different locations. The high PM_{10} concentration was attributed to diesel driven vehicles. In another study in Trans-Gomti area, during peak traffic hours (11.00 a.m.–1.00 p.m.) the recorded PM_{10} level was 499 $\mu g/m^3$. The highest PM_{10} level (990 $\mu g/m^3$) was observed at the most crowded crossing with most traffic density (6723 vehicle/h) and least (150 $\mu g/m^3$) at low traffic density crossing with least vehicular load (52 vehicle/h). This investigation revealed that the Trans-Gomti area is mainly polluted with PM_{10} and advised to ban diesel driven vehicles in the city areas to cut the PM_{10} level within the permissible limit (Verma et al. 2003). Vehicular exhaust is one of the major reasons of particulate contamination, which affects the air quality and the health. Uttar Pradesh State Road Transport Corporation (UPSRTC) introduced bus services under the banner "Lucknow Mahanagar Parivahan Sewa" on different routes of Lucknow city. The Green Peace Report in 2016 has highlighted that in 20 cities of Uttar Pradesh, from where the data was collected by Pollution Control Board, the PM_{10} concentration was higher than the annual average of 60 $\mu g/m^3$ as suggested under NAAQS. PM_{10} concentrations in Gaziabad, Barielly, Allahabad, Kanpur, Agra, Lucknow, Varanasi and Sonebhadra were respectively 258, 240, 250, 201, 186, 169, 145 and 132 $\mu g/m^3$ for year 2015. A comprehensive observation of the data suggests that the PM_{10} level has been dangerously high throughout the year for from October 2015 to September 2016, with October to February being the most polluted months when the PM_{10} reached to 400 $\mu g/m^3$ (http://ueppcb.uk.gov.in/files/ Ambient_Air_Quality_2015__(2).pdf). Some of the recent episodes of air pollution in Lucknow are as follows:

1. In December, 2015 AQI of the city reached to 489. The AQI between 401 and 500 has been categorized as severe for the exposed population (http://timesofindia. indiatimes.com/city).
2. Lucknow recorded a "very poor" air quality condition on Diwali night, 2018 with $PM_{2.5}$—(International Business Times).
3. With an average $PM_{2.5}$ concentrations of 138$\mu g/m^3$, Lucknow was placed at 7th position out of ten most polluted cities of the world, according to WHO's latest report in 2018.

4. Lucknow climbed up to the position of second most polluted city in the country on November 28, 2018 with the AQI 'very poor (Times of India). As per the data released by the Central Pollution Control Board, the AQI of the city was 363.

2.5.3   Objectives of the Study

The study was conducted in fifteen urban houses of Lucknow city from 2012 to 2014 to assess PM_{10} and $PM_{2.5}$ concentration to analyze seven heavy metals viz. Fe, Zn, Cu, Pb, Mn, Ni and Cr associated with PM_{10} and $PM_{2.5}$. Principal component analysis and enrichment of elements/metals from outdoor sources were also performed to identify the sources of metals in particulate matter as a part of source apportionment.

Selected Microenvironments
Fifteen urban houses were selected on the basis of house characteristics, traffic rush and population distribution and categorized under three microenvironments as:

1. Unplanned or densely populated
2. Well planned
3. Roadside

Houses in densely populated microenvironment were constructed according to old architectural designs. They were closely built in congested narrow lanes. Parking space was very limited and mostly people parked their vehicles outside the house. Frequent power cuts were observed in these localities and people usually used diesel driven generators as power back up. Outdoor characteristics were marked by crowded market places. There were frequent waste dumping and incineration activities and piles of garbage sighted. In contrast to the architectural pattern of the houses in densely populated microenvironment, those in well planned microenvironment were relatively newly constructed. The houses mostly had parking spaces within the house premises. Small parks and abundant greenery marked the surroundings. Electricity supply was also regular and most of the households relied on invertors for power back up. Roadside microenvironment was marked by heavy traffic rush as the houses were situated along the highways experiencing heavy vehicular load throughout the day and reaching to the peak between 9:00–11:00 a.m. and 4:00–7:00 p.m. Mainly natural ventilation was observed in the houses and they were constructed according to modern architectural patter. For outdoor sampling, the instrument was placed either on roof top or on the verandah as per convenience. House characteristics are summarized in Table 2.5.

Table 2.5 House characteristics in different microenvironments

Microenvironment	Sampling site	Site description
Well planned	LDA	Proper new houses with ventilation, Negligible traffic flow
	Gomtinagar	Developed area with proper ventilation and greenery
	Mahanagar	Moderate flow of traffic
	Indiranagar	Less population, new houses, parks and low vehicle traffic
	Jankipuram	New Houses, with low vehicle traffic and shops
Densely populated	Chowk	Dense population, Congested area with least greenery. Old type of houses, lots of small shops
	Rajajipuram	Dense population, bad roads, many small schools, low vehicular traffic
	Muftiganj	Congested area with no proper roads, Approximately 20 year old congested houses
	Triveni Nagar	Busy area with old types of commercial shops and houses
	Aminabad	Very Busy market area (shops are present inside houses).
Roadside	I.T. Chowraha	Heavy traffic flow during day time
	Bakshi ka Talab	Heavy diesel traffic flow 24 h
	Balaganj	Bus and truck flow mainly in daytime
	Alambagh	Heavy traffic flow 24 h. Mainly due to buses
	Mushi Pulia	Traffic rush from Buses and trucks mainly in daytime

2.5.4   Sampling and Analytical Method

The study was conducted for a span of two years viz. March 2012 to Feb 2014. Particulate matter was measured through 24 h continuous monitoring in the selected houses representing three distinct microenvironments. The purpose of continuous monitoring was to cover major household activities and their influence on the indoor particulate variation as well as the effect of outdoor activities. The instrument was set up in the living area where people spend maximum of their time. PM_{10} and $PM_{2.5}$ samples for chemical analysis were collected with fine particulate dust sampler (APM 550, Envirotech). The air inlet has a circular symmetrical hood designed to keep out rain, insects and very large particles. Inlet section leads to an Impact stage with trap particles larger than 10 microns. For the sampling of $PM_{2.5}$ a well shaped (WINS) Impactor can be attached to the down tube. It is designed to trap medium size (between 2.5 and 10 micron) particles. To avoid sampling error due to bouncing of small size particulate from impaction surface, a 37 mm diameter GF/A (Glass Fibre) paper immersed in silicon oil is used. APM 550 used oil-less rotary pump to produce the suction pressure and critical flow control or office (as recommended by USEPA) for

maintaining a constant air-flow rate of 1 m^3/hr or 16.7 L/min. The particles were collected on 47 mm diameter, 2 μm pore size polytetrafluoroethylene Whatmann filters. Glass fiber filters are cheap and have been used in many studies previously for determination of metals in coarse particle. Sampling was done at a height of 1 m from ground level for 24 h with frequency of once a week at all sites, that is 4 times a month, 16 times a season. The air inlet hood of collection sampler was kept at a height of 1–1.5 m above the ground level to simulate the human breathing zone. The instrument was set at least 1 m away from any significant pollution sources.

Analysis of Heavy Metals
Gravimetric Analysis

The filters were weighed thrice before and after sampling using balance (Citizen, Model No. ISO 900:2000) with a sensitivity limit of ± 0.2 mg. Before weighing, the samples were equilibrated in desiccator at 20–30 °C and relative humidity of 30–40% in a humidity controlled room for 24 h. Field blank filters were collected to reduce gravimetric bias due to filter handling while sampling and afterward. Filters were handled only with tweezers coated with Teflon to reduce the possibility of contamination. After weighing, samples were kept in fridge till further analysis. It was assumed that particulate matter accumulated on filter papers was evenly distributed over the entire area.

Chemical Analysis

The exposed filter was digested in 6–8 mL of analytical grade (AR) (Merck) HNO_3 on hot plate at 40–60 °C for 90 min. The solution was diluted up to 50 mL with distilled de-ionized water and preserved in polypropylene bottles till analysis. Analysis of the metals was done on Atomic Absorption Spectrophotometer (AAS) (Perkin Elmer, AAnalyst 100) (Kulshrestha et al. 2014).

Quality Assurance

The particulate sampler was calibrated in the beginning and at the end of sampling. Filter in the wins impactor was usually changed after 72 h of sampling. The minimum detection limit of the heavy metals is given in Table 2.6.

Table 2.6 Detection limit of the heavy metals

Metal	Detection limit (mg/L)
Pb	0.10
Zn	0.018
Ni	0.063
Fe	0.060
Cr	0.055
Mn	0.052
Cu	0.077
Cd	0.60

2.6   Results and Discussion

Average concentrations of particulate matter are given in Tables 2.7, 2.8 and 2.9 in summer, rainy and winter seasons. The results revealed that average yearly indoor concentration of PM_{10} and $PM_{2.5}$ were 79 $\mu g/m^3$ and 59 $\mu g/m^3$ respectively in well planned houses, whereas houses in densely populated areas had an average yearly indoor concentrations of 90 $\mu g/m^3$, and 60 $\mu g/m^3$ for PM_{10} and $PM_{2.5}$ respectively. Roadside houses had an average yearly concentration of 100 $\mu g/m^3$ and 66.4 $\mu g/m^3$ respectively for PM_{10} and $PM_{2.5}$. Roadside houses were found to have maximum particulate contamination followed by densely populated and well planned, Indoor particulate concentration was found to be higher than the WHO limits. Overall analysis showed that roadside microenvironment was most polluted, having the poorest air quality.

2.6.1   Analysis of Heavy Metal Concentration in Particulate Samples

Fe, Zn, Pb, Cr, Ni, Cu and Mn were analyzed in PM_{10} and $PM_{2.5}$ samples with the help of AAS in all the three microenvironments. Fe was found to have highest concentration in both particulates $PM_{2.5}$. The levels of assessed metals in all the three microenvironments were found to be in the following order:

Well planned microenvironment—Fe > Zn > Pb > Cr > Ni > Cu > Mn
Densely populated microenvironment—Fe > Cr > Zn > Pb > Ni > Cu > Mn
Roadside microenvironment—Fe > Pb > Zn > Cr > Ni > Cu > Mn
Overall trend of heavy metals—Fe > Zn > Pb > Cr > Ni > Cu > Mn

The average concentration of heavy metals is given in Tables 2.10, 2.11 and 2.12. The sum of the seven analyzed metals ΣMetals was calculated and the trend exceeded up to five times at the roadside houses than the threshold limits. Excess of Pb in the roadside houses can be attributed to mixing of residual Pb in soil and its re-suspension in the air due to heavy vehicles. It was also observed that the concentration of Ni associated with $PM_{2.5}$ was much higher in the months of November and December. Low temperature and relative humidity causes dilution of pollutants in these seasons. Higher concentration of Ni is a major concerning issue as people can easily get exposed to it by inhalation or dermal contact. Atmospheric concentrations of metals did not differ substantially between each microenvironment. In densely populated microenvironment Cr was in higher concentration because of coal and kerosene burning in winter months. Nickel finds its way into the ambient air as a result of the combustion of coal, diesel oil and fuel oil, the incineration of waste and sewage, and miscellaneous sources. Tobacco smoke in the form of gaseous nickel carbonyl, stainless steel in kitchen, inexpensive jewelry utensils also contributes to lower level of nickel (Kulshrestha et al. 2014). Although Zn and Cu are essential elements, their

Table 2.7 Particulate concentration in summer season ($\mu g/m^3$)

Microenvironment	Pollutant	March			April			May			June		
		Indoor	Outdoor	I/O	Indoor	Outdoor	I/O	Indoor	Outdoor	I/O	Indoor	Outdoor	I/O
Densely populated	PM_{10}	82 ± 3.2	102 ± 7.4	0.8	74 ± 0.06	144 ± 7.7	0.40	90 ± 6.8	115 ± 7.1	0.74	84 ± 4.9	178 ± 5.1	0.47
Well planned		62 ± 4	94 ± 5	0.63	67 ± 9	107 ± 21	0.63	87 ± 13	121 ± 14	0.76	78 ± 18	103 ± 12	0.84
Roadside		82 ± 3.2	121 ± 7.8	0.91	104 ± 0.06	184 ± 7.1	0.57	127 ± 6.8	191 ± 7.1	0.66	124 ± 4.9	186 ± 5.8	0.7
Densely populated	$PM_{2.5}$	42 ± 1.6	89 ± 1.1	0.61	34 ± 0.04	79 ± 0.2	0.43	53 ± 1.7	92 ± 0.03	0.65	55 ± 0.8	82 ± 0.6	0.67
Well planned		62 ± 9	84 ± 26	0.66	64 ± 30	156 ± 14	0.41	57 ± 23	109 ± 35	0.52	51 ± 8	75 ± 34	0.85
Roadside		72 ± 9	98 ± 26	1.0	74 ± 30	86 ± 14	0.86	69 ± 21	119 ± 35	0.64	71 ± 9	89 ± 34	0.77

Table 2.8 Particulate concentration in rainy season ($\mu g/m^3$)

Microenvironment	Pollutant	July			August			September			October		
		Indoor	Outdoor	I/O	Indoor	Outdoor	I/O	Indoor	Outdoor	I/O	Indoor	Outdoor	I/O
Densely populated	PM_{10}	133 ± 42	163 ± 28	0.54	77 ± 28	112 ± 36	0.69	68 ± 42	124 ± 12	0.55	62 ± 21	96 ± 17	0.65
Well planned		82 ± 42	95 ± 90	0.91	67 ± 8	82 ± 3	0.81	59 ± 19	101 ± 20	0.58	61 ± 43	97 ± 63	0.63
Roadside		89 ± 32	91 ± 90	0.95	78 ± 12	108 ± 40	0.72	92 ± 11	117 ± 26	0.79	71 ± 52	109 ± 74	0.65
Densely populated	$PM_{2.5}$	103 ± 1.7	113 ± 62	0.51	56 ± 3.5	61 ± 0.09	0.92	45 ± 3.2	83 ± 1.1	0.54	54 ± 2.1	75 ± 0.8	0.72
Well planned		57 ± 13	45 ± 67	1.22	39 ± 1.3	62 ± 1.8	0.63	54 ± 1.7	82 ± 2.1	0.65	56 ± 2.7	74 ± 3.7	0.76
Roadside		47 ± 7.3	86 ± 7.5	0.55	64 ± 3.8	81 ± 4.6	0.79	44 ± 2.8	89 ± 5.7	0.49	79 ± 7.9	88 ± 7.1	0.9

Table 2.9 Particulate concentration in winter season ($\mu g/m^3$)

Microenvironment	Pollutant	November			December			January			February		
		Indoor	Outdoor	I/O	Indoor	Outdoor	I/O	Indoor	Outdoor	I/O	Indoor	Outdoor	I/O
Densely populated	PM_{10}	118 ± 17	165 ± 23	0.72	102 ± 40	153 ± 17	0.67	109 ± 30	163 ± 13	0.67	81 ± 9	104 ± 84	0.78
Well planned		103 ± 51	312 ± 46	0.33	98 ± 27	247 ± 38	0.4	89 ± 13	156 ± 12	0.57	96 ± 36	129 ± 61	0.74
Roadside		108 ± 13	232 ± 54	0.46	107 ± 43	215 ± 28	0.50	102 ± 26	205 ± 17	0.5	114 ± 40	212 ± 36	0.54
Densely populated	$PM_{2.5}$	64 ± 0.4	94 ± 0.07	0.68	70 ± 1.2	82 ± 0.04	0.85	72 ± 0.03	83 ± 0.5	0.87	71 ± 2.1	87 ± 0.9	0.82
Well planned		66 ± 5.65	105 ± 7.1	0.63	69 ± 6.9	97 ± 1.1	0.71	53 ± 7.1	64 ± 2.6	0.83	80 ± 6.4	95 ± 2.1	0.84
Roadside		75 ± 11.2	81 ± 13.4	0.93	69 ± 12.1	81 ± 17.7	0.85	74 ± 18.7	94 ± 14.1	0.79	54 ± 9.4	89 ± 8.4	0.61

Table 2.10 Average mass concentration ($\mu g/m^3$) of metals in PM_{10} and $PM_{2.5}$ at well planned microenvironment

Months	Fe		Pb		Mn		Cu		Ni		Cr		Zn	
	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$
January	8.33 ± 2.18	4.20 ± 1.79	0.02 ± 0.13	0.98 ± 0.16	0.01 ± 0.02	0.05 ± 0.03	0.10 ± 0.02	0.50 ± 0.22	0.02 ± 0.04	0.24 ± 0.29	0.03 ± 0.12	0.48 ± 0.63	0.21 ± 0.19	1.69 ± 0.21x
February	9.36 ± 3.52	5.73 ± 2.72	0.01 ± 0.17	0.73 ± 0.21	0.21 ± 0.24	0.06 ± 0.05	0.01 ± 0.03	0.23 ± 0.17	0.32 ± 0.26	0.36 ± 0.28	0.97 ± 0.54	0.72 ± 0.50	0.05 ± 0.08	2.45 ± 0.98
March	6.79 ± 1.51	3.68 ± 1.23	0.04 ± 0.02	0.80 ± 0.23	0.16 ± 0.23	0.07 ± 0.05	0.03 ± 0.03	0.16 ± 0.14	0.11 ± 0.15	0.38 ± 0.24	0.06 ± 0.17	0.50 ± 0.03	0.96 ± 0.54	1.13 ± 0.78
April	1.32 ± 0.21	4.11 ± 1.09	0.03 ± 0.11	0.62 ± 0.22	0.32 ± 0.24	0.06 ± 0.04	0.03 ± 0.02	0.24 ± 0.13	0.21 ± 0.24	0.43 ± 0.22	0.72 ± 0.53	0.62 ± 0.13	0.04 ± 0.03	1.39 ± 0.11
May	0.18 ± 0.03	1.33 ± 2.01	0.03 ± 0.04	0.82 ± 0.24	0.13 ± 0.05	0.06 ± 0.08	0.02 ± 0.02	0.12 ± 0.14	0.15 ± 0.16	0.34 ± 0.22	0.09 ± 0.11	0.12 ± 0.03	0.02 ± 0.52	2.45 ± 0.68
June	0.39 ± 0.06	1.32 ± .23	0.06 ± 0.14	0.79 ± 0.24	0.09 ± 0.34	0.03 ± 0.04	0.02 ± 0.05	0.25 ± 0.13	0.36 ± 0.28	0.31 ± 0.24	0.21 ± 0.23	0.18 ± 0.32	0.02 ± 0.03	1.43 ± 0.58
July	0.13 ± 0.17	1.45 ± 1.74	0.02 ± 0.01	0.93 ± 0.09	0.09 ± 0.22	0.03 ± 0.02	0.04 ± 0.02	0.12 ± 0.14	0.13 ± 0.12	0.35 ± 0.25	0.13 ± 0.13	0.42 ± 0.43	0.04 ± 0.52	1.39 ± 0.15

(continued)

Table 2.10 (continued)

Months	Fe		Pb		Mn		Cu		Ni		Cr		Zn	
	PM$_{10}$	PM$_{2.5}$	PM$_{10}$	PM$_{2.5}$	PM$_{10}$	PM$_{2.5}$	PM$_{10}$	PM$_{2.5}$	PM$_{10}$	PM$_{2.5}$	PM$_{10}$	PM$_{2.5}$	PM$_{10}$	PM$_{2.5}$
August	0.29 ± 0.08	3.82 ± 2.12	0.04 ± 0.15	0.35 ± 0.35	0.14 ± 0.23	0.02 ± 0.04	0.04 ± 0.02	0.22 ± 0.16	0.15 ± 0.26	0.43 ± 0.38	0.08 ± 0.24	0.35 ± 0.35	0.05 ± 0.08	2.35 ± 0.28
September	0.21 ± 0.03	3.48 ± 1.63	0.02 ± 0.05	0.82 ± 0.13	0.05 ± 0.45	0.02 ± 0.04	0.04 ± 0.01	0.14 ± 0.15	0.42 ± 0.14	0.28 ± 0.22	0.02 ± 0.17	0.25 ± 0.57	0.16 ± 0.34	1.33 ± 0.08
October	1.90 ± 0.45	1.78 ± 0.60	0.35 ± 0.48	0.75 ± 0.20	0.07 ± 0.02	0.07 ± 0.03	0.02 ± 0.08	0.23 ± 0.17	0.45 ± 0.33	0.43 ± 1.24	0.01 ± 0.01	0.09 ± 0.07	0.19 ± 0.03	2.10 ± 0.95
November	1.19 ± 0.78	1.05 ± 1.41	0.26 ± 0.06	0.91 ± 0.56	0.12 ± 0.15	0.04 ± 0.03	0.01 ± 0.10	0.39 ± 0.50	0.06 ± 0.14	0.09 ± 0.07	0.03 ± 0.02	1.16 ± 1.53	0.21 ± 0.22	0.90 ± 0.83
December	2.72 ± 0.21	2.76 ± 0.71	0.03 ± 0.07	0.89 ± 0.77	0.09 ± 0.07	0.08 ± 0.06	0.05 ± 0.07	0.06 ± 0.02	0.06 ± 0.21	0.68 ± 0.81	0.08 ± 0.14	1.35 ± 1.54	0.65 ± 0.22	0.42 ± 0.54

Table 2.11 Average mass concentration ($\mu g/m^3$) of metals in PM_{10} and $PM_{2.5}$ at densely populated microenvironment

Months	Fe		Pb		Mn		Cu		Ni		Cr		Zn	
	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$
January	3.18 ± 2.531	3.19 ± 0.81	0.11 ± 0.06	0.51 ± 0.16	0.12 ± 0.26	0.08 ± 0.07	0.08 ± 0.09	0.14 ± 0.29	0.02 ± 0.05	0.01 ± 0.02	0.71 ± 0.81	1.83 ± 0.71	1.64 ± 1.53	0.59 ± 0.03
February	4.45 ± 2.61	4.65 ± 1.24	0.18 ± 0.07	0.89 ± 0.24	0.01 ± 0.06	0.02 ± 0.05	0.08 ± 0.06	0.50 ± 0.06	0.33 ± 0.17	0.05 ± 0.09	1.61 ± 0.98	1.53 ± 0.34	0.10 ± 0.05	0.66 ± 0.17
March	2.54 ± 1.73	1.63 ± 0.23	0.08 ± 0.09	0.76 ± 0.29	0.10 ± 0.09	0.20 ± 0.45	0.06 ± 0.09	0.48 ± 0.05	0.01 ± 0.02	0.21 ± 0.14	0.56 ± 0.33	0.54 ± 0.67	1.32 ± 1.48	1.74 ± 1.25
April	1.32 ± 0.11	2.1 ± 1.9	0.23 ± 0.11	0.42 ± 0.22	0.22 ± 0.14	0.02 ± 0.01	0.03 ± 0.72	0.41 ± 0.33	0.22 ± 0.28	0.33 ± 0.32	0.73 ± 0.17	0.45 ± 0.12	0.01 ± 0.03	1.31 ± 0.12
May	0.18 ± 0.08	1.43 ± 2.01	0.33 ± 0.54	0.62 ± 0.24	0.34 ± 0.35	0.01 ± 0.03	0.12 ± 0.12	0.22 ± 0.34	0.12 ± 0.19	0.44 ± 0.62	0.02 ± 0.28	0.21 ± 0.03	0.03 ± 0.51	2.1 ± 0.08
June	0.39 ± 0.01	1.22 ± .22	0.56 ± 0.64	0.79 ± 0.24	0.08 ± 0.36	0.04 ± 0.08	0.32 ± 0.005	0.05 ± 0.43	0.39 ± 0.09	0.25 ± 0.25	0.28 ± 0.24	0.21 ± 0.32	0.01 ± 0.01	0.33 ± 0.28
July	0.13 ± 0.27	1.15 ± 1.74	0.08 ± 0.01	0.63 ± 0.09	0.03 ± 0.21	0.02 ± 0.02	0.06 ± 0.01	0.12 ± 0.44	0.10 ± 0.12	0.33 ± 0.26	0.05 ± 0.13	0.34 ± 0.17	0.04 ± 0.56	1.27 ± 0.12

(continued)

Table 2.11 (continued)

Months	Fe		Pb		Mn		Cu		Ni		Cr		Zn	
	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$
August	0.29 ± 0.08	3.32 ± 2.12	0.08 ± 0.1	0.25 ± 0.35	0.11 ± 0.22	0.02 ± 0.04	0.01 ± 0.01	0.32 ± 0.16	0.25 ± 0.26	0.06 ± 0.38	0.05 ± 0.22	0.68 ± 0.41	0.05 ± 0.46	2.13 ± 0.18
September	0.21 ± 0.03	3.18 ± 1.33	0.01 ± 0.04	0.42 ± 0.13	0.02 ± 0.41	0.01 ± 0.03	0.04 ± 0.03	0.34 ± 0.15	0.32 ± 0.12	0.06 ± 0.11	0.02 ± 0.09	0.16 ± 0.78	0.14 ± 0.24	1.13 ± 0.009
October	1.95 ± 1.66	0.39 ± 0.86	0.11 ± 0.05	0.88 ± 0.79	0.04 ± 0.05	0.03 ± 0.03	0.06 ± 0.02	0.04 ± 0.28	0.13 ± 0.16	0.33 ± 0.56	0.85 ± 0.54	2.59 ± 1.42	0.59 ± 0.72	1.69 ± 0.63
November	2.77 ± 0.91	1.84 ± 0.77	0.15 ± 0.06	0.31 ± 0.05	0.07 ± 0.04	0.05 ± 0.09	0.02 ± 0.03	0.05 ± 0.60	0.09 ± 0.06	0.72 ± 0.24	0.53 ± 0.47	2.07 ± 0.87	0.08 ± 0.15	0.34 ± 0.12
December	2.73 ± 1.55	2.24 ± 0.67	0.21 ± 0.55	0.32 ± 0.08	0.10 ± 0.39	0.03 ± 0.21	0.03 ± 0.12	0.66 ± 0.16	0.13 ± 0.18	0.43 ± 0.52	0.74 ± 0.68	1.01 ± 0.92	0.11 ± 0.01	0.73 ± 0.63

Table 2.12 Average mass concentration (µg/m³) of heavy metals in PM_{10} and $PM_{2.5}$ at roadside microenvironment

Months	Fe		Pb		Mn		Cu		Ni		Cr		Zn	
	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$
January	2.67 ± 0.21	2.24 ± 0.28	2.04 ± 1.03	1.11 ± 1.23	0.12 ± 0.23	0.05 ± 0.3	0.10 ± 0.16	0.48 ± 0.68	0.03 ± 0.01	0.65 ± 0.56	0.11 ± 0.06	1.13 ± 0.97	0.74 ± 0.53	1.58 ± 0.63
February	1.76 ± 0.32	0.87 ± 0.51	1.24 ± 1.56	1.07 ± 0.25	0.08 ± 0.05	0.05 ± 0.23	0.07 ± 0.04	0.39 ± 0.03	0.02 ± 0.02	0.56 ± 0.36	0.08 ± 0.04	0.67 ± 0.07	0.51 ± 0.69	0.75 ± 0.01
March	1.21 ± 0.23	0.87 ± 0.23	1.36 ± 0.33	1.22 ± 1.13	0.11 ± 0.09	0.02 ± 0.02	0.09 ± 0.16	0.09 ± 0.16	0.06 ± 0.09	0.59 ± 0.23	0.11 ± 0.06	0.49 ± 0.36	0.08 ± 0.6	0.44 ± 0.32
April	1.32 ± 0.11	0.52 ± 0.9	1.24 ± 0.19	1.32 ± 0.16	0.31 ± 0.10	0.03 ± 0.12	0.13 ± 0.32	0.44 ± 0.33	0.23 ± 0.45	0.32 ± 0.25	0.22 ± 0.13	0.42 ± 0.53	0.43 ± 0.03	1.29 ± 0.21
May	0.18 ± 0.08	0.18 ± 0.14	1.01 ± 0.26	1.09 ± 0.16	0.13 ± 0.02	0.04 ± 0.12	0.45 ± 0.03	0.22 ± 0.44	0.05 ± 0.16	0.09 ± 0.25	0.09 ± 0.81	0.32 ± 0.43	0.12 ± 0.12	1.31 ± 0.68
June	0.39 ± 0.01	0.82 ± 0.16	0.91 ± 0.31	0.86 ± 0.21	0.13 ± 0.09	0.08 ± 0.21	0.24 ± 0.24	0.23 ± 0.24	0.34 ± 0.23	0.04 ± 0.24	0.11 ± 0.03	0.28 ± 0.12	0.32 ± 0.03	2.03 ± 0.13
July	0.13 ± 0.27	0.1 ± 0.06	1.32 ± 1.4	0.91 ± 0.93	0.03 ± 0.11	0.03 ± 0.32	0.24 ± 0.24	0.24 ± 0.56	0.09 ± 0.12	0.35 ± 0.25	0.03 ± 0.12	0.12 ± 0.33	0.03 ± 0.51	1.41 ± 0.11

(continued)

Table 2.12 (continued)

Months	Fe		Pb		Mn		Cu		Ni		Cr		Zn	
	PM$_{10}$	PM$_{2.5}$	PM$_{10}$	PM$_{2.5}$	PM$_{10}$	PM$_{2.5}$	PM$_{10}$	PM$_{2.5}$	PM$_{10}$	PM$_{2.5}$	PM$_{10}$	PM$_{2.5}$	PM$_{10}$	PM$_{2.5}$
August	0.29 ± 0.08	0.42 ± 0.19	0.98 ± 1.23	0.83 ± 0.19	0.05 ± 0.02	0.38 ± 0.13	0.12 ± 0.32	0.22 ± 0.15	0.06 ± 0.24	0.43 ± 0.38	0.05 ± 0.21	0.55 ± 0.55	0.03 ± 0.01	2.32 ± 0.21
September	0.21 ± 0.03	0.14 ± 0.32	0.97 ± 0.94	0.95 ± 0.11	0.06 ± 0.12	0.08 ± 0.06	0.24 ± 0.41	0.15 ± 0.12	0.04 ± 0.12	0.08 ± 0.42	0.01 ± 0.17	0.25 ± 0.97	0.36 ± 0.44	1.05 ± 0.18
October	0.14 ± 0.02	0.12 ± 0.07	1.45 ± 0.67	0.67 ± 0.34	0.01 ± 0.04	0.09 ± 0.05	0.08 ± 0.03	0.74 ± 0.64	0.05 ± 0.04	0.08 ± 0.05	0.10 ± 0.01	0.31 ± 0.08	0.07 ± 0.13	0.73 ± 0.40
November	1.95 ± 0.51	1.87 ± 0.91	1.98 ± 0.36	0.68 ± 1.24	0.09 ± 0.31	0.04 ± 0.23	0.07 ± 0.18	0.24 ± 0.09	0.02 ± 0.08	0.11 ± 0.25	0.08 ± 0.04	0.55 ± 0.04	0.53 ± 0.32	0.61 ± 0.07
December	7.42 ± 1.6	2.67 ± 0.3	2.18 ± 0.76	1.87 ± 1.3	0.26 ± 0.13	0.12 ± 0.37	0.02 ± 0.05	0.34 ± 0.40	0.06 ± 0.04	0.61 ± 0.41	0.08 ± 0.33	0.87 ± 0.85	1.24 ± 0.64	2.27 ± 0.77

excessive concentration in food and feed plants are of great concern because of their toxicity to humans and animals (Kulshrestha et al. 2014).

2.6.2   Correlation Among Heavy Metals

Univariate Pearson correlations were determined using SPSS 11 (Tables 2.13, 2.14 and 2.15) to find association among heavy metals so as to identify the common sources of these metals. The positive correlation have been shown by * sign.

Correlation of Metals in PM$_{10}$
In well planned microenvironment, Fe, Zn and Mn showed good correlation with each other probably originating from common sources including the outdoor dust. Some other known outdoor sources of Zn include lubricating oils and tyres of automobiles while re-suspended road dust is a major source of Fe and Mn. Pb, Cu, Ni and Cr depicted correlation with each other, which may be due to common indoor sources like paint and household dust. In densely populated microenvironment Ni, Cr and Fe showed good correlation. Common sources of Ni and Cr in these houses may be the combustion of polluting fuels such as kerosene and diesel various proposes (Joshi et al. 2017).

Correlation of Metals in PM$_{2.5}$
Pb, Ni, Cr and Mn showed positive correlation in roadside microenvironment which can be attributed to vehicular emission along with re-suspension of soil dust. Fe, Cu, Ni, Cr and Pb showed positive correlation owing to construction work, as Fe is used for pillar framing and the roofing. Cement and paint are known sources of Pb. In another study on similar pattern (Mahish et al. 2015) it was found that concentration of Pb and other trace elements was several times higher in PM$_{10}$ sample near a cement plant. Cr showed a good correlation with Ni (0.95) attributed to the combustion of coal and other inferior fuels. Zn showed correlation with Mn and Pb in PM$_{10}$ mainly due to vehicular exhaust and its infiltration. Pb, Mn, Ni and Cr showed good correlation with PM$_{2.5}$ whereas Fe, Mn and Zn showed good correlation with PM$_{10}$ at roadside microenvironment. House dust originated from outdoor or indoor sources was identified as a potent source of particulate concentration. Activities like wear and tear of tyres, burning of oil, abrasion of mechanical parts and oil lubricants etc. also contribute to the release of metals. Pb, Cu, Ni and Cr showed good inter-correlation indicating their mutual originating sources.

Table 2.13 Inter correlation between metals at well planned microenvironment

Metals	Fe	Pb	Mn	Cu	Ni	Cr	Zn	PM$_{10}$	PM$_{2.5}$
Fe	1								
Pb	−0.68	1							
Mn	0.99*	−0.69	1						
Cu	−0.85	0.80*	−0.79	1					
Ni	−0.98	0.80*	−0.96	0.92*	1				
Cr	−0.5	0.97*	−0.5	0.71*	0.66*	1			
Zn	0.97*	−0.68	0.99*	−0.72	−0.93	−0.49	1		
PM$_{10}$	0.74*	−0.46	0.80*	−0.45	−0.69	−0.32	0.82*	1	
PM$_{2.5}$	0.59*	0.77*	0.66*	0.18	0.86*	0.75*	0.09	0.69*	1

The sign * represents values which are positive.

Table 2.14 Inter correlation between metals at densely populated microenvironment

Metals	Fe	Pb	Mn	Cu	Ni	Cr	Zn	PM$_{10}$	PM$_{2.5}$
Fe	1								
Pb	−0.46	1							
Mn	0.3	−0.32	1						
Cu	0.43	0.54*	−0.59	1					
Ni	−0.11	0.77*	−0.01	−0.54	1				
Cr	0.64*	0.53*	0.71*	−0.29	0.24	1			
Zn	0.03	−0.16	0.13	0.17	−0.36	−0.4	1		
PM$_{10}$	0.51*	−0.22	0.52*	0.83*	−0.49	−0.1	0.54*	1	
PM$_{2.5}$	−0.29	0.07	−0.22	0.29	−0.25	0.16	0.12	0.09	1

Table 2.15 Inter correlation between metals at roadside microenvironment

Metals	Fe	Pb	Mn	Cu	Ni	Cr	Zn	PM$_{10}$	PM$_{2.5}$
Fe	1								
Pb	0.51*	1							
Mn	0.59*	−0.32	1						
Cu	0.74*	−0.26	−0.2	1					
Ni	0.79*	0.67*	−0.88	0.24	1				
Cr	0.94*	0.51*	−0.82	0.54*	0.95*	1			
Zn	−0.23	−0.79	0.69*	0.45	−0.76	−0.51	1		
PM$_{10}$	0.57*	0.62*	0.23	0.22	0.52*	0.59*	−0.05	1	
PM$_{2.5}$	−0.12	0.59*	0.51*	0.33	−0.24	−0.24	0.83*	0.56*	1

2.6.3 Principal Component Analysis for Heavy Metals Associated with PM_{10} and $PM_{2.5}$ and Identification of Their Sources

PCA was used to identify the key sources of the heavy metals associated with the particulate concentrations. Varimax rotated factor analysis was done to identify three chief sources of the heavy metals associated with the particulate matter. Only those factors were included in the matrix whose Eigen value was > than one ranging from 3.11 to 1.18 in the three microenvironments. Mass distribution of the metals was considered for Factor Analysis.

Factor Analysis in Well Planned Microenvironment
In PM_{10} samples Cu and Cr with 34% variance represented Factor 1 and road dust was identified as their main source. Fe, Mn, Ni and Cr represented Factor 2 with 31% variance which was linked to solid waste dumping and burning (Kulshrestha et al. 2014). Zn and Pb with 27% variance represented Factor 3 and household dust was their main source. Household paint was identified as a chief source of Pb (Wang et al. 2000). These three factors attributed to 92% of the sources responsible for heavy metal contamination as represented in Fig. 2.4a. In $PM_{2.5}$ samples Cu represented Factor 1 with 19% variance and road dust was attributed as its major source. Fe, Mn and Cr with 36% variance represented Factor 2 due to solid waste incineration (Zhang et al. 2008). Pb and Ni represented Factor 3 with 32% variance and household dust and some indoor activities were attributed as their major sources. The results obtained from the PCA analysis were well justified by inter-correlation of metals (Fig. 2.4b).

Factor Analysis in Densely Populated Microenvironment
Ni and Cr with 42% variance represented Factor 1 owing to fuel combustion (Massey et al. 2013). Fe and Cu with 29% variance represented Factor 2. Construction activities and road dust were identified as their major sources. Pb and Zn with 25% variance
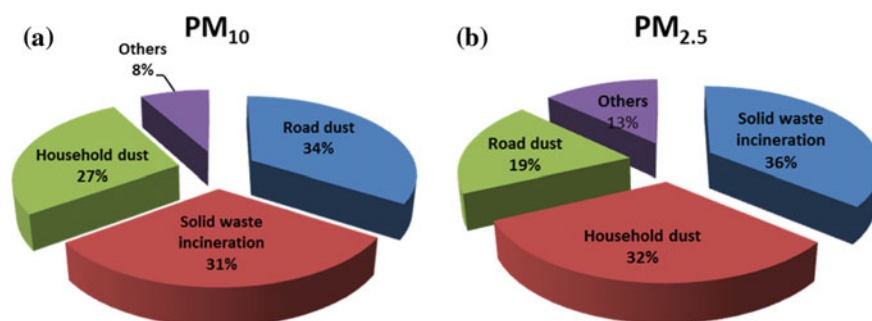
Fig. 2.4 a–b Pie diagram showing source distribution of particle constituent at well planned microenvironment in **a** PM_{10}, **b** $PM_{2.5}$
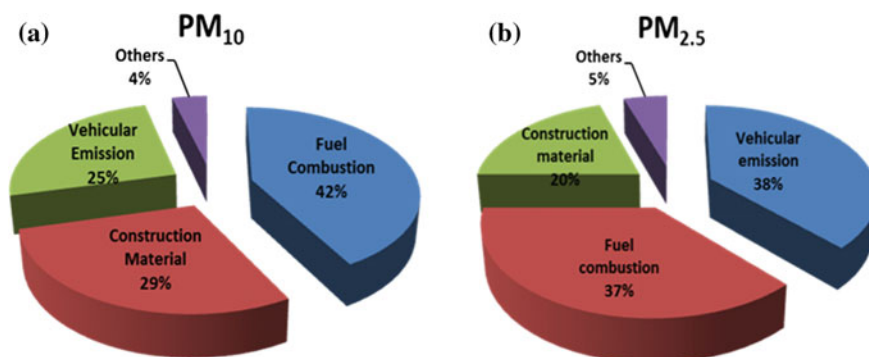
Fig. 2.5 a–b Pie diagram showing source distribution of particle constituent at densely populated microenvironment in **a** PM_{10}, **b** $PM_{2.5}$

represented Factor 3 attributing to vehicular exhaust and its infiltration (Park and Dam 2010). These three factors contributed to 96% of source contribution of metals in PM_{10} (Fig. 2.5a). In $PM_{2.5}$ samples three main factors explained 80% of the source contribution of heavy metals. Pb with 38% variance represented Factor 1 and was attributed to vehicular exhaust. Fe, Ni and Cr with 37% variance represented Factor 2 owing to combustion. Fe, Cu and Cr with 5% variance represented Factor3 being associated with construction activities (Fig. 2.5b).

Factor Analysis in Roadside Microenvironment
Two main factors analyzed in this microenvironment contributed to 93% of heavy metal concentration in PM_{10} samples (Fig. 2.6a). Fe and Zn with 58% variance represented Factor 1 attributed to infiltration of outdoor dust. Pb, Mn, Cu, Ni, and Cr represented Factor 2 with 35% variance owing to household dust. Cr is also found to be emitted from domestic heating (Homa et al. 2016) while Mn and Pb contamination can be sourced from smoking and cooking. Zn is usually emitted from abrasion of tyres while resuspended road dust is a potential source of Fe. In $PM_{2.5}$ samples the two main factors explained 79% of source contribution (Fig. 2.6b). Pb, Cu, Ni and Cr with 58% variance represented Factor 1 and household dust was identified as their main source. In PM_{10} Fe, Mn and Zn represented Factor 1 with 21% variance and was accredited to seeped outside dust.

2.6.4 Enrichment of Heavy Metals from Indoor Sources

Enrichment factor (EF) was calculated for the heavy metals to know their origin. Indoor metals may have originated from outdoor air or from indoor sources. A comparison between the ambient metallic concentrations with that of indoors, is of utmost significance which can be performed by calculating enrichment ratios for different
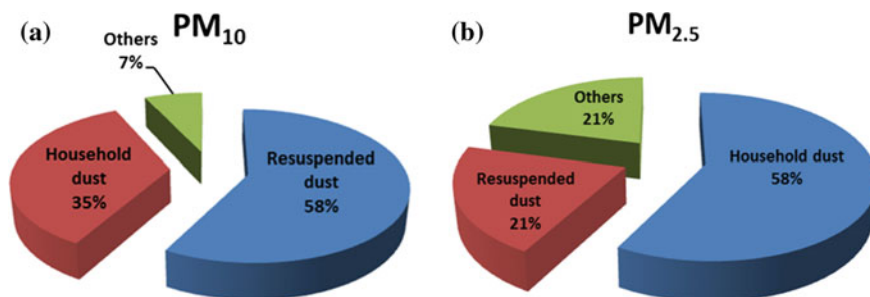
Fig. 2.6 a–b Pie diagram showing source distribution of particle constituent at Roadside microenvironment in **a** PM$_{10}$, **b** PM$_{2.5}$

elements taking into account, both indoor and outdoor concentrations. The concentrations are usually normalized to an element considered as being the most ambiguous indicator of source material. The enrichment factor was calculated by estimating indoor outdoor ratios of different metals which are usually normalized (Rahn 1976). In this study particulate concentration was taken as reference on an assumption that all the particulate matter in the air was of outdoor origin. The enrichment factor can be calculated as:

$$EF_{INDOOR} = \{X_{INDOOR}/PM_{INDOOR}\}/\{X_{OUTDOOR}/PM_{OUTDOOR}\} \quad (2.3)$$

Where, X is the concentration of the metal under investigation. Elements with EFs close to unity are likely to have originated from outdoor sources and are considered to be non-enriched. Elements with enrichment factors significantly greater than one are considered as enriched and likely have their origin other than outdoor air.

Well planned microenvironment—At well planned microenvironment only Ni was found to be enriched in PM$_{10}$ samples with enrichment factor (EF) 2.59. While in PM$_{2.5}$ samples Pb, Ni and Zn were found to have enrichment factor greater than one i.e. 1.14, 1.10 and 1.21 respectively and therefore have some indoors sources as well. Presence of Pb may be due to wall dust indoors at these sites which contains paint. Ni and Zn are found to have additional sources indoors at all sites. This might be due to the use of cosmetics, household utensils and burning cigarettes (Kulshrestha et al. 2014).

Densely populated microenvironment—At the densely populated microenvironment no metal in PM$_{10}$ sample showed EF < 1 indicating their origin from outdoor sources. In PM$_{2.5}$ samples Cu, Ni, Cr and Zn were found to have EFs greater than one viz. 4.39, 3.26, 1.21 and 1.43 respectively depicting their origin within the household. Pb associated with both sizes of particulate matter was likely to be emitted from outdoor sources. Pb was enriched at the roadside and well planned microenvironments whose major source was wall dust containing paint. Pigments in paints include oxides of Fe, Mn, Cr and Sb along with lead antiminate, cadmium selenide, lead, zinc and barium chromates. Pb is also used as a corrosion inhibitor

in "lead-free" paints. Ni and Zn were emitted from indoor sources. Their probable sources are cosmetics, household utensils and cigarette smoke. High levels of indoor Zn have also been reported in a previous study (Feng and Barratt 1993). Goyal et al. (2012) Cr concentration has been associated with Ni and Zn indicating their mutual indoor source (Goyal et al. 2012). Cr, enriched in $PM_{2.5}$ samples, was found to have additional sources which were believed to be due to usage of kerosene/oil. In the other two microenvironments, Cr was mainly emitted from outdoor sources. Fe in all the microenvironments associated with PM_{10} and $PM_{2.5}$ had EF less than one and believed to be originated from outdoor sources.

Roadside microenvironment—At roadside microenvironment in PM_{10} samples Pb, Cu and Zn were found to be enriched with EFs 1.60, 1.70 and 1.12 respectively, while in $PM_{2.5}$ samples Pb, Mn, Cu, Ni and Zn were enriched having EFs 1.27, 2.79, 1.06, 1.28, and 3.69 respectively and hence it was concluded that the metals originated from some indoors sources in addition to outdoor infiltration.

2.7 Recommendations

Air pollution is a major environmental risk to human beings. By adopting suitable measures, nation can decrease the risk of stroke, heart disease, lung cancer, and both chronic and acute respiratory diseases which are associated with air pollution. Policies and investments supporting cleaner transport, energy-efficient homes, industry and improved l waste management can play key roles in curbing ambient pollution which directly affects the level of indoor pollution. Outdoor pollution control is possible through a concerted action taken by the public, policy makers working in sectors like transport, energy, waste management and urban planning and academicians. A few instances adopted in transport, urban planning, power generation and industry that reduce air pollution:

1. Facilitation of clean energy sources at affordable prices for cooking, heating and lighting.
2. To improve indoor air quality focus should be on increasing energy efficiency of buildings.
3. Use of low-emission fuels and renewable power means co-generation of heat and power and distributed energy production like solar panels should be promoted.

Indoor air pollution is a direct consequence of ambient pollution levels. The problem can be dealt with by a synchronized effort made by the government, industries, research and academia. The government should carve stringent policies and work in close coordination with various agencies like CPCB to chalk down a robust plan leading to the development of indoor air quality policies. Creating mass awareness and sensitizing both rural and urban areas of the country and it should be taken up as a national campaign. The focal theme of the awareness can be centred on the use of better quality fuels which are affordable at the same time. Promotions of clean energy options like solar energy lit lamps than the indigenously built kerosene lamps

Fig. 2.7 Summary of an efficient health risk assessment study

should be done in masses. Usage of biogas and improved cooking stoves should be made available for users at a nominal price. Government should consult with stakeholders including environment scientists, engineers and public health experts to set guidelines and standards. The role of construction industries is also crucial for adopting measures to check indoor air pollution from the word go. Better building material like low VOC emitting materials, radon-resistant building practices can lessen the risks of lung cancer. Finally identification of the gaps in literature and its thorough assessment can be taken up by researchers and academicians. Long term exposure assessment studies and their health consequences should be worked upon to come up with concrete conclusions about the extent of damage done by the poor quality of indoor air to the human health. Research programmes highlighting gaps in research and adoption of novel measures to address the challenge are needed to be studied. Collaborations should be made with international agencies where IAQ guidelines are already in exercise. Researchers may help government in creating mass public awareness operations to apprise public about the indoor air quality allied issues and appropriate actions to control them (Goyal et al. 2012) (Fig. 2.7).

2.7.1 Modeling of Indoor Air Pollution

Air pollution modeling is used to assess the precision to which air pollutants can be measured in accurate quantities which is required for the accurate prediction of the level of pollution. An indoor air quality prediction model generally relates indoor pollutant concentration with factors like ventilation sources, source origin of the pollutants, various geometric parameters and sink. Through pollution modeling, accurate and desired function of concentration, such as peak concentration for a particular set of condition can be predicted through mathematical simulation rather than prediction by manual monitoring. Indoor air quality models are helpful in prediction of pollutants present indoors and their association with ambient pollutant concentrations, indoor-outdoor air-exchange rates, and sources of indoor pollutants. Pollutants may trespass indoors through infiltration or ventilation. Whereas indoor pollutants arise from point or diffuse sources. The pollutants may be transported and dispersed though a wide region. The first step in indoor modeling involves establishing a statement of the mass balance concerning the pollutant under consideration.

When air passes through a filter at a rate q_0 through a structure of volume V, some of the air is recirculated through another filter at a rate q_1, and air infiltrates the structure at a rate q_2. Each filter is characterized by a factor $F \equiv (C_{inlet} - C_{outlet})/C_{inlet}$. The pollutant level is anticipated to be constant all over. The indoor and outdoor pollutant concentrations at time t are C and C_0. The rate at which the pollutant is added to the indoor air is S. The rate at which the pollutant is removed from the air owing to internal sinks is R. In this case, a suitable initial equation is:

$$V \frac{dC}{dt} = q_0 C_0 (1 - F_0) + q_1 C (1 - F_1) + q C_0 - (Q_0 + q_1 + q_2)C + S - R$$

$$(2.4)$$

The decay rate is a function of C, however, in modeling indoor air quality, the sink rate is often assumed to be constant. Accurate values of the ventilation parameters are usually more difficult to determine. Without forced ventilation, air exchange is primarily due to infiltration; in most forced-ventilation systems (which are balanced so that negative pressures are not created inside the building), the rate of infiltration is negligible, as compared to the forced-ventilation rate. In view of the uncertainties associated with many of the parameter values and the difficulty of doing otherwise, compartments have been widely used in modeling indoor air quality. A compartment is a region within which spatial variations in pollutant concentrations can be neglected. The main motive of indoor air quality modeling is to study the association between the indoor and outdoor pollutant concentration and the effect of geometric and ventilation characteristics of a building. To have an overall picture of the indoor environmental conditions, an efficient study must include the corresponding outside concentrations, geometric parameters, ventilation parameters sink and strength of the source. These factors are vital for a mass balance based model.

2.8 Conclusion

Air in urban cities has become highly polluted with pollutants crossing the standards set by the World Health Organization (WHO). Among all the air pollutants, particulate matter can cause significant health damage, specifically particles that are smaller than $10\,\mu m$. The present study conducted in three urban microenvironments of Lucknow city concluded that indoor air quality was worse in roadside houses having highest particulate concentrations. At all the three location Fe was found to be dominating element followed by Zn and Pb. Contaminated household dust was identified as one of the main sources of toxic heavy metals. From the PCA it was fond that vehicular emission, re-suspended dust and solid waste incineration were some of the common sources contributing the particulate matter. Crude fuel combustion was identified as another important factor. The metals were found to be enriched in both sizes of particulate matter. There is a need to assess the heavy metal contamination in different environmental components. Studies have reported the origin of

heavy metals through source apportionment of particulate matter, however nothing substantial has been proposed that enables optimal control and regulation of emission of these heavy metals in the atmosphere to reduce impact on health. Economic factors and cost effective methods for monitor and control of these heavy metals need consideration.

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