

Chapter 5

Vehicle-Generated Heavy Metal Pollution in an Urban Environment and Its Distribution into Various Environmental Components



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Abstract Pollution caused by vehicles and its rapidly growing number is a serious concern all over the world. Vehicular pollution is primarily known for emitting various kinds of organic and inorganic gaseous pollutants in to the atmosphere, but recent studies show that vehicles are one of the chief sources of creating heavy metal pollution in an urban environment via processes like exhaust of diesel and petrol, corrosion of metallic parts, engine wear, tyre and brake pad wear and road surface degradation due to vehicular movement. Studies show that apart from fuel burning, tyre and brake wear particles lead the contribution of heavy metals into an urban environment. Due to easy availability and low cost, two wheelers dominate the road traffic and become a major source of air pollution in most of the developing countries. Heavy metals emitted in ambient air ultimately get deposited on other environmental component like hydrosphere and lithosphere which ultimately affect flora and fauna living in it. Some heavy metals are able to create toxicity at low level of exposure, and metals like nickel, cadmium and chromium are able to produce carcinogenicity in humans. Meteorological and geographical conditions of an area play a major role in distribution and deposition of heavy metals. There is an urgent need to make an effective environmental management plan for urban areas which include promotion of new technologies, adaption of biofuels, green belt development and public participation.

Keywords Vehicular pollution · Heavy metal · Tyre and brake pad · Meteorological · Management plan

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5.1 Introduction

Problem of environmental pollution is increasing day by day in both developed and developing countries due to urbanization and industrialization. The trend of migration of people from villages to towns and cities has been seen all over the world as cities are concentrated centres of production, consumption and waste disposal. The proportion of the world's population living in urban areas, which was less than 5% in 1800, increased to 47% in 2000 and is expected to reach 65% by the year 2030 (United Nations 2006). Urbanization of an area includes good infrastructure, presence of various other amenities and well-connected routes of transportation. Roads are important infrastructure of an urban area that contributes a major part in stimulating social and economic development of a country. The USA boasts the world's largest road network, followed by China and India, the world's two most populous countries. Because of their versatility, flexibility and low initial cost, motorized road vehicles overwhelmingly dominate the markets for passenger and freight transport throughout the world. Calculating the total number of motor vehicles on the planet is an inexact science, but the number is growing rapidly. The automotive trade journal *Ward's AutoWorld* had estimated that the total crossed 1 billion vehicles sometime during 2010. The vehicles include passenger cars; light-, medium-, and heavy-duty trucks; and buses but not off-road or heavy construction vehicles. Just 40 years ago, in 1970, the world total was only a quarter of a billion vehicles, a number that took 85 years to achieve. The 1970 total doubled in just 16 years to 500,000,000 by 1986. It took 24 more years to double again to the current 1 billion. By some projections, the world could house as many as 2.5 billion vehicles by 2050. The estimated total number of vehicles in India is more than 200 million up to the year 2016.

Although road transportation speeds up the development of a nation, on the other side, it is inserting large amount of toxic pollutants into the environment. It is reported that vehicles are responsible for more than 40% of the total air pollution and this percentage increases up to 70–80% for megacities in developing nations (Bharti et al. 2017). Vehicles mainly emit two kinds of pollutants: (1) gaseous pollutants and (2) particulate pollutants. Gaseous pollutants basically come out via fuel exhaust and further categorized into inorganic and organic gas pollutants. Oxides of sulphur (SO_2 , SO_3 , etc.), oxides of nitrogen (NO_2 , NO , N_2O , etc.), oxides of carbon (CO_2 , CO , etc.), ammonia and ozone are well-known inorganic gaseous pollutants, whereas aliphatic and aromatic hydrocarbons like benzene, benzo(a) pyrene, aldehydes, ketones, etc. come under organic gaseous pollutants. Particulate matter which is emitting out from vehicles in solid and liquid form is a mixture of various inorganic and organic pollutants, but heavy metals are of particular concern. Tearing, wearing of tyre and brake pad, corrosion of metallic parts and paints and fuel emission are mainly responsible for particulate matter pollution which carry various kinds of heavy metals in its chemical composition. Heavy metals are found

ubiquitous in nature and generated via both natural and anthropogenic sources; second they show a tendency to accumulate various environmental components and are able to magnify their concentration as we move upwards in trophic level. Heavy metals are defined as metallic elements that have a relatively high density compared to water. With the assumption that heaviness and toxicity are interrelated, some heavy metals are able to induce toxicity at low level of exposure.

The primary source of heavy metals in the environment is lithosphere. Heavy metals occur naturally in the earth's crust and may be released into the soil and atmosphere via process of weathering and volcanic eruption, respectively, which are two main natural sources of heavy metals in the environment. Although natural sources contribute significant amount of heavy metals, anthropogenic activities are mainly responsible for heavy metal contamination in an urban environment. In an urban environment, heavy metals derived mainly from vehicular and industrial emissions. Industrial sources include ore extraction and mining industries, coal-based thermal power plants, pesticide industries, textile industry, oil and petroleum refinery, battery industry, etc., whereas vehicles generate heavy metals via two main ways, i.e. exhaust and non-exhaust ways. After coming out from different vehicular sources, heavy metals remain suspended in atmosphere and ultimately get deposited into surrounding environment via dry and wet deposition. Deposition and distribution in turn depends on many factors and meteorological conditions. Heavy metals show tendency to accumulate in plants and animals and ultimately create toxicity in human beings. There were various clinical studies that have been done for toxicity analysis of various heavy metals. The aim of this review paper is to summarize the sources of vehicular-generated heavy metals and its distribution over other environmental component.

5.2 Sources of Vehicular-Generated Heavy Metals in Urban Areas

Urban environment may receive heavy metal loads from different sources but one of the most important being vehicle emissions (Table 5.1). Vehicles generate heavy metals into the atmosphere mainly via exhaust and non-exhaust vehicular emissions. Exhaust category mainly includes petrol and diesel emission, and non-exhaust category includes wearing and tearing of various vehicular components like tyre and brake pad wear, engine wear and corrosion of metallic parts and paints which basically create particulate matter pollution. Apart from exhaust and non-exhaust category, road surface degradation and road paint corrosion also contribute heavy metals into the atmosphere (Lindgren 1996; Legret et al. 2005). The US EPA highlights 21 toxic substances that can mainly be assigned to road traffic. Some heavy metals such as Pb, Cu, Sb, Cd, Ni or Zn are among them. Main vehicular sources which emit heavy metals are as follows.

Table 5.1 Concentration of heavy metal in the world soil

Metal ($\mu\text{g g}^{-1}$)	Soil	
	typical	Range
Ni	40	10–1000
Pb	10	2–2000
Cr	100	5–3000
Cu	20	2–100
Cd	0.06	0.01–0.07
Zn	50	10–300
Mg	–	–
Mn	850	100–4000
Fe	38,000	7000–550,000

Source: Bowen 1979

5.2.1 Fuel Exhaust

Diesel and gasoline are two main fossil fuels which are used to power most of the road vehicles because petroleum fuels carry much more energy than other substances. These two fossil fuels are basically made from hydrocarbons, but various potentially toxic heavy metals are present in crude oil. Presence of heavy metals in petroleum product depends on two main factors: first the geological location in which crude oil is being formed where metals found in rocks are absorbed into the crude oil; second heavy metals in crude oil are the introduction of drilling mud fluids into the oil well during crude oil extraction (NNPC/PTI 1987; Stanley 2002). The heavy metals in the crude oil distribute themselves into the petroleum fractions and invariably act as contaminants.

When fuel burn carbon and hydrogen combine with oxygen to make carbon dioxide gas and water, the energy that held the molecules together is released as heat. Along with various gaseous emissions, metals are emitted to the ambient air via exhaust pipe or catalytic converter. Arsenic, cadmium, chromium, copper, mercury, nickel, lead, selenium and zinc are the main heavy metals emitted from the burning of diesel and gasoline fuel. The gasoline used as fuel in automobiles may contain metalloids and metallic elements such as Pb, Cu, Zn, Ni, Fe, As, Cd, Hg, Se and Ti (Fig. 5.1). These elements are derived from the raw product but can also be introduced as additives during production or contaminants during storage (Ozaki et al. 2004).

5.2.2 Brake Pad Wear and Tyre Wear

Brakes and tyres are used to stop and accelerate vehicles, respectively. Wearing and tearing of tyres and brake pad take place due to friction between road surface and vehicular component, during braking and acceleration process. The tyres are basically made from rubber which are fitted around a metallic frame, and brake pads are

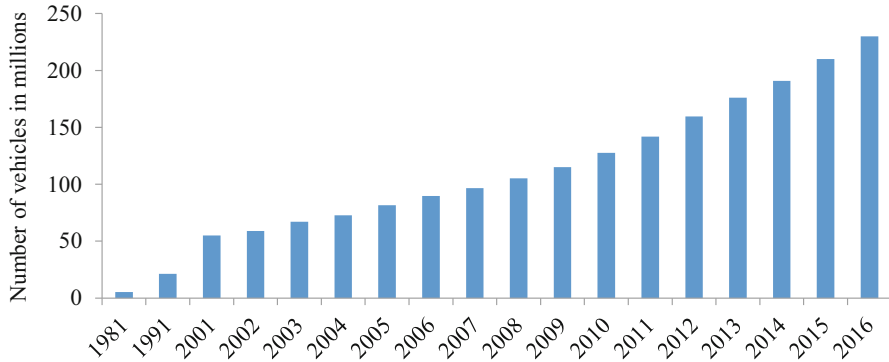


Fig. 5.1 Total number of vehicles across India from 1981 to 2016

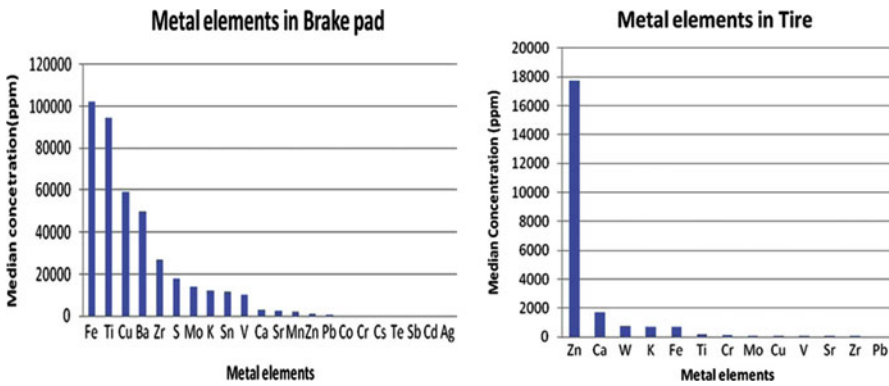


Fig. 5.2 Metal concentration (ppm) in brake pads and tyres analysed by XRF in 2008. (Source: Apegyei et al. 2011)

combination of non-metallic, semimetallic to fully metallic materials (Figs. 5.2 and 5.3). Detailed analyses of tyre wear dust have been conducted by various researchers which show that heavy metals like Fe, Zn, Cd, Cr, Cu, Co, Hg, Mo, Ni and Pb were associated with dust from tyre wear in significant amount (Fukuzaki et al. 1986; Fauser et al. 1999; Adachia and Tainoshob 2004; Schauer et al. 2006; Hjortenkrans et al. 2007). Zn was the most abundant heavy metal from tyre wear, and its high concentrations resulted from the use of ZnO and ZnS to the tyre during vulcanization (Smolders and Degryse 2002; Ozaki et al. 2004). Another source of heavy metals from vehicles is wear particles from brake pad linings. During braking, brakes are exposed to extensive heat from friction, which results in the emission of particles. The worn particles of tyre and brake pad dispersed directly into the environment. It has been investigated that brake pads are a major source of metal emission such as Fe, Ti, Cu, Ba, Zr, Sb, Mo, K, Sn, V, Ca, Sr, Mn, Zn, Pb and Co, and tyre wear is an important source for Zn, Ca, W, K, Fe, Ti, Cr, Cu, etc. (Apegyei et al. 2011).

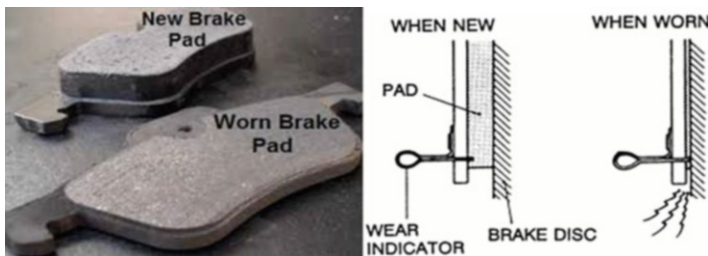


Fig. 5.3 Image of new and worn brake pad

Adachia and Tainoshob (2004) and Hjortenkrans et al. (2007) have reported that brake dust mainly contained Fe, Cu, Sb, Ba, Al, Si, S, Ti, Zn, Ni, Cr and Pb and a small amount of Cd. The extent of wearing and tearing of tyre and brake pad depends on the characteristics of tyres, types of vehicles, condition of road surface, vehicle operation mode, road design, etc.

5.2.3 Engine Oil and Engine Wear

Engine, or motor, oil is designed to lubricate the inner components of internal combustion engines, as well as to protect them against corrosion and keep them cool while in use. It's made from two main elements: base stock and additives. The base stock commonly makes up 95% of the solution and is either made from petroleum, synthetic chemicals or a mixture of the two. The base stock is responsible for lubricating an engine's moving parts and removing built-up heat. The additives, meanwhile, account for roughly 5% of the oil, and it is these chemicals that are responsible for finely controlling oil viscosity and lubricity, as well as protecting engine parts against wear. For example, zinc dialkyldithiophosphate (ZDDP) is a frequently used additive for preventing wear, while magnesium sulphonates help the oil to break down impurities and engine sludge. Table 5.2 shows the common sources of heavy metals used in gasoline or diesel engine oil.

5.2.4 Road Abrasion

Road abrasion takes place due to the friction which generates between tyres and road surface of vehicles due to continuous movement and braking process. Due to continuous abrasion, road surface particles loosen out and ultimately came out into the environment. Asphalts are significant sources of Ni and As in road dust (Ozaki et al. 2004). It has been reported that the concentrations of Ni and Zn in road bitumen were higher than in raw bitumen (Gadd and Kennedy 2000). It should be noted that more tyre abrasion occurs when a vehicle drives on a concrete motorway compared

Table 5.2 Common sources of the elements in a gasoline or diesel engine oil

Aluminium	Pistons, bearings, cases (heads and blocks)
Chromium	Rings, a trace element in steel
Iron	Cylinders, rotating shafts, the valve train and any steel part sharing the oil
Copper	Brass or bronze parts, copper bushing, bearings, oil coolers, also an additive in some gasoline engine oils
Lead	Bearings
Tin	Bearings, bronze parts, piston coatings
Molybdenum	Antiwear additive, coating on some new rings (washes off as break in occurs)
Nickel	Trace element in steel
Manganese	Trace element, additive in gasoline
Silver	Trace element
Titanium	Trace element
Potassium	Antifreeze inhibitor, additive in some oil types
Boron	Detergent/dispersant additive, antifreeze inhibitors
Silicon	Airborne dirt, sealers, gaskets, antifreeze inhibitors
Sodium	Antifreeze inhibitors, additive in some gasoline engine oils
Calcium	Detergent/dispersant additive
Magnesium	Detergent/dispersant additive
Phosphorus	Antiwear additive
Zinc	Antiwear additive
Barium	Detergent/dispersant additive

with an asphalt surface so fuel consumption becomes higher on concrete surface (Duong and Lee 2011). Bitumen and mineral filler materials in asphalt road surfaces contain different heavy metal species, including Cu, Zn, Cd and Pb (Winther and Slento 2010). Road abrasion is influenced by various factors: vehicle speed, climate, moistness of the road and type of asphalt and share of heavy-duty vehicles (Johansson and Burman 2006).

5.3 Deposition and Distribution of Heavy Metals in Various Environmental Components

The pathways of heavy metal transportation into the soil and water environment are dry and wet deposition processes and runoff water. Deposition takes place on any surface where particulate matter gets a chance to settle down. It settles down may be on exposed soil surface, water surface, plants or any physical material. Before deposition heavy metal-laden particles travel long distances due to particle size of the pollutant, wind direction and wind velocity (Reinirkens 1996; Barbosa and Hvitved-Jacobsen 1999). The relationship between the metal content of urban soils and distance from the roads has been widely investigated, and many studies have shown that metal concentrations decrease exponentially with the distance from

roads. It is well documented that soil pollution by heavy metals is generally concentrated in the first few metres to tens of metres on either side of the road pavement and then sharply decreases with distance from the road (Motto et al. 1970; Harrison et al. 1985; Turer et al. 2001; Blok 2005; Li 2005). The degree of contamination of pollutants in an environment depends on factors such as site-specific pollution sources (i.e. industrial activities), the topography and the architectural design of the location (i.e. narrow roads, high density of high buildings, open spaces) and the presence and density of the surrounding vegetation (Chronopoulos et al. 1997). The following are the main factors which affect the heavy metal distribution in an urban environment:

1. Climatic and geographical factors
2. Road-related factors
3. Vehicle-related factor
4. Traffic-related factors

5.3.1 Climatic and Geographical Factors

Metrological conditions like wind velocity, wind direction, frequency and intensity of rainfall profiles, duration of fog conditions and morphology of the soil and vegetation cover have known to play their part in the dispersion of contaminants (Piron-Frenet et al. 1994; Melaku et al. 2008). Wind patterns strongly influences the spatial dispersal of heavy metal. Contamination usually declines within 20 m, and the pattern of decline is influenced by prevailing wind patterns (Haqus and Hameed 1986). In addition to point sources that spread metals within a restricted area, deposition of redistributed metals in soil and dust and long-range atmospheric transport of metals have led to increased soil metal concentrations in many urban areas today, including areas located away from major roads and industrial activities (Paterson et al. 1996; Ljung et al. 2006). Indeed, long-range atmospheric transport of metals has been recorded for the Eastern Mediterranean basin regions, derived from as far as the Northern Africa, Central and Western Europe and the Sahara Desert (Chester et al. 1996; Koulousaris et al. 2009). Rain washes out the atmospheric pollutants so that ultimately concentration of heavy metals also decreases in soil and atmosphere. Speed of rain and runoff water displaces the pollutants away from the highways. Rainwater also helps in leaching heavy metals in deeper soil. Winter and foggy condition concentrates vehicular emission near the sources, and dispersal of heavy metals is minimal. Transport rate and travel distance of metals increase substantially when they reach aquatic environments. In the terrestrial environment, metals can be localized in the soil, either close to the surface or deep below the surface, if pollution levels in the past exceeded those in the present.

Geographical condition of a region also contributes towards the dispersal of pollutants. In hilly areas dispersal is not very frequent due to mountain restrictions, but in desert-like condition, dispersal of pollutants increases. If there is vegetation

cover along the highways and roads, then the dispersal and mobility of heavy metals are also restricted. The centre and inner side of city experiences ‘canyon’ effect of buildings, which has a direct influence on dilution and dispersion pathways of the heavy metals released from motor vehicles (Namdeo et al. 1999). Particles tend to fall out within the urban roadway ‘canyon’ resulting in higher heavy metal levels than found alongside motorways, where higher traffic densities are observed.

5.3.2 Road-Related Factors

Roadway factors affecting the pollution levels are carriage way width, lateral clearance, medians, shoulder width, smoothness and surface material of road, etc. As the road width increases, the manoeuvrability to movement of the vehicles will be increased, which results in the reduction of pollutants. Dividers reduce the obstruction caused by the opposing vehicles, which results in the reduction of number of accelerations and decelerations so that the fuel consumption will be minimized, thus reducing the emission levels of pollutants (Harrison et al. 1985; Wigington et al. 1986; Munch 1993). The road having more twist and turns and tunnels (mainly in hilly terrain) enhances the load of pollutants than the roads found in plain areas. The difference in tyre and road wear materials will be mainly associated with the difference in the road surface materials such as asphalt and concrete (Duong and Lee 2011). More tyre abrasion occurs when vehicles drive on a concrete highway than on an asphalt highway because the concrete surface is rougher than the asphalt surface. Also, the increased energy consumption of vehicles driving on a rough concrete highway versus an even asphalt highway could result in increased heavy metal concentrations in the road dust from the concrete highway.

5.3.3 Vehicle Factor

The age of the vehicle, its condition and servicing frequency, type of engine (2-stroke, 4-stroke), speed of vehicle and vehicle miles travelled come under the vehicle factor category. The older vehicles will emit more pollutants than a newer one, if they are not maintained properly. Vehicles with 4-stroke engine would produce lesser emissions than 2-stroke engine. Similarly, vehicles with catalytic converter will emit less pollutant. Most of the by-products of automobiles comprise of different fraction particles. These fractions include the ultrafine particles which are formed in the engines and tailpipes, fine particles produced mainly by chemical reactions and coarse particles which are formed mechanically by the abrasion of road materials, tyres and brake linings (Olukanni and Adebisi 2012). Though the use of unleaded gasoline has caused a subsequent reduction in fuel emissions of Pb, it may still occur in exhaust gas and come from worn metal alloys in the engine (Snowdon and Birch 2004). The highly elevated concentrations of the heavy metals in road dust

from the highways probably result from the influence of the high emissions from increased engine emissions and tyre and road abrasion by high-speed vehicles (Duong and Lee 2011).

5.3.4 Traffic Factor

Traffic factors such as traffic volume, traffic congestion, average speed of the flow, etc. come under this category. When the traffic volume is more, the greater vehicular load will lead to greater emissions of heavy metals from vehicles. The contamination of heavy metals especially Pb, Cd and Cu in roadside soil is related to the traffic density on the roads (Olajire and Ayodele 1997; Kartal 1992). The levels of nickel, cadmium, copper and zinc were also reported to correlate with traffic density (Fergusson et al. 1980; Thornton 1988; Narin et al. 1997; Narin and Soylak 1999). Traffic composition also contributes significantly to the pollution levels because emission rate varies for different types of vehicle. Hence, the same amount of traffic volume with different vehicular compositions produces different amounts of pollutants. Speed limits also affect the amount of pollution because faster drive consequently increases fuel burning. Therefore, introducing lower speed limits on motorways is expected to cut both fuel consumption and pollutant emissions. Therefore, one of the major reasons behind the high heavy metal levels within inner cities is the 'stop-start' pattern that is often observed. Changes in traffic flow patterns and congestion in specific inner city areas (roundabouts, traffic lights and junctions) result in the possible release of many heavy metals, both from combustion particles and the wear and tear of the vehicular component especially tyres, brake linings, etc. (Charlesworth et al. 2003; Ewen et al. 2009).

5.4 Impacts of Vehicular-Generated Heavy Metals on Urban Environment

Heavy metals emitted from various vehicular processes primarily get into the atmosphere, thus creating particulate air pollution like particles which are less than 10 micron metre and particles less than 2.5 micron metre and ultrafine particles less than 0.1 micron metre. These heavy metal-laden particulate matters react with other chemicals and form secondary air pollutants like smog. These particulate matters also influence the local weather and in winter season reduce the visibility. Contaminated street dust can potentially affect an urban air environment via resuspension in air. Road dust resuspension has proven to be one of the most important sources for airborne particulate trace metals in urban areas (Pereira et al. 2007). Dust-borne heavy metals accumulate in topsoil due to atmospheric deposition by sedimentation, impaction and interception and ultimately disturb the nutrient dynamics (Li et al. 2007; Lu

et al. 2009). In general, influences between air and soil pollution are mutual. Just as the atmosphere can transfer a large amount of heavy metals into urban soils through precipitation (Ritter and Rinefierd 1983; Patel et al. 2001), soil dust can also contribute to the concentration of heavy metals in the air (Chen et al. 1997).

Excessive accumulation of heavy metals in soil may lead to elevated heavy metal uptake by crops, which in turn can affect food quality and safety (Muchuweti et al. 2006). On the soil, these pollutants can be transported to the aerial parts of vegetation (Wiseman et al. 2013). Some heavy metals are considered persistent bioaccumulative toxins and may be bioavailable in ecosystems (Basta et al. 2005). In the case where plants and animals are raised for human consumption, high levels of metal accumulation may pose health hazards to humans.

Sediment and dust transported and stored in the urban environment have the potential to provide considerable loadings of heavy metals to receiving water and waterbodies, particularly with changing environmental conditions (Morrison et al. 1990). There are only few measurements of pollution patterns in combination with leaching characteristics of highly polluted roadside soils (Li 2005; Hjortenkrans et al. 2008; Saeedi et al. 2012).

Due to the non-biodegradability and long half-lives that make heavy metals more persistent in the environment, their accumulation in the urban soil has a harmful effect on environmental quality including the biota and human beings in the long term (Zhuang et al. 2009). Heavy metals adhering to or absorbed by dust particles can enter the human body though through three main pathways (Ferreira-Baptista and De Miguel 2005; Shi et al. 2011):

- Ingestion of dust particles
- Inhalation of dust particles
- Dermal contact with dust particles

Pb, Cr, Zn, Cd and other toxic metals will continue to accumulate in urban environment due to their non-biodegradability and long residence time; thus they are known as ‘chemical time bombs’. In particular, more concern needs to be shown for children than adults because of their frequent hand-to-mouth activities, higher absorption rate from the digestion system and haemoglobin sensitivity to toxic metals (Meza-Figueroa et al. 2007; Zheng et al. 2010). Children daily ingest, on average, 50–200 mg of soil via hand-to-mouth behaviour (Calabrese et al. 1999; Oomen et al. 2003). Children and the elderly, whose immune systems are either underdeveloped or age compromised as well as the inadvertent ingestion of significant quantities of dust through hand-to-mouth pathways, are more vulnerable to toxicity (Rasmussen et al. 2001). Pollutants attached to surface dusts can be transferred to the surrounding aquatic environment with runoff and can cause a serious threat to the water environment and human health (Jartun et al. 2008; Zhao et al. 2011).

There are many published studies that have documented the adverse effects of lead in children and the adult population. In children, these studies have shown an association between blood level poisoning and diminished intelligence, lower intelligence quotient (IQ), delayed or impaired neurobehavioral development, decreased

hearing acuity, speech and language handicaps, growth retardation, poor attention span and anti-social and diligent behaviours (Amodio-Cocchieri et al. 1996; Kaul et al. 1999; Litvak et al. 1998).

Cadmium, chromium and nickel compounds are classified as human carcinogens by several regulatory agencies. The International Agency for Research on Cancer and the US National Toxicology Program have concluded that there is adequate evidence that cadmium is a human carcinogen. Epidemiological investigations have reported respiratory cancers in workers occupationally exposed to Cr (VI)-containing compounds.

5.5 Conclusion

Vehicular emission is of the main source of heavy metal pollution in any urban environment. Heavy metals come out from vehicles via exhaust and non-exhaust sources. Heavy metals primarily get introduced in atmosphere and ultimately get deposited in various environmental components mainly via dry and wet deposition methods. The distribution and dispersion of heavy metals chiefly depends upon wind velocity, rain events and intensity of rain, humidity, topography and vegetation cover of an area, etc. In biological system heavy metals get accumulated via bioaccumulation and biomagnification processes. Contamination of air, water and soil system ultimately affects the human health and especially young children especially below 5 years of age. There is an urgent need for comprehensive epidemiological studies to show how heavy metals are affecting human's different functional systems and use this information in order to provide policy tools for air quality. It is also important to quantify the geogenic and anthropogenic contribution of heavy metals because there is still insufficient information about the differentiation between anthropogenic and geogenic dust particles.

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