



Heavy Metal Pollution in the Environment: Impact on Air Quality and Human Health Implications

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Abstract

Atmospheric pollution of heavy metals (HMs) has become a considerably huge cause of concern due to its greater toxicity, persistence nature, and bioaccumulative behavior. Although most of the HMs are natural environmental constituents, its biochemical equilibrium and geochemical processes have been altered by indiscriminate anthropogenic activities owing to the demand for better quality of life with modern conveniences. More than 80% of people who live in metropolitan areas are reportedly exposed to poor air quality, per the World Health Organization (WHO). As a consequence, the urban population has experienced a wide range of adverse health effects, including cancer and damage to essential organs as well as cardiovascular and pulmonary inflammation and acute respiratory disorders. This chapter presents an overview of the atmospheric heavy metal pollution, its impact on the air quality, and human health implications. A detailed discussion has been made on the sources, pathways, and fate of HMs in the environment followed by their toxicological effects on human health.

Keywords

Heavy metals · Air quality · Atmospheric pollution · Toxicology · Health impacts

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4.1 Introduction

Heavy metals (HMs) are a major environmental hazard across the world (Zhu et al. 2020). Because of their nonbiodegradability, bioaccumulation, environmental stability, persistence, and biotoxicity, HMs constitute a significant environmental danger to living beings and environments (Khan et al. 2019; Zhang et al. 2019). Natural (geological weathering, atmospheric precipitation, wave erosion, wind, and bioturbation) and anthropogenic (rapid industrialization, urbanization, agricultural runoff, and transportation) activities both contribute to the escalation of elevated air pollution levels (Nour et al. 2019; Kahal et al. 2020). However, rampant industrialization, rising energy demand, and the indiscreet utilization of the natural resources are the major causes of intensifying the global environmental pollution issues (Gautam et al. 2016; Briffa et al. 2020). Inorganic and organic constituents, gaseous pollutants, organometallic compounds, nanoparticles, and radioactive isotopes are major pollutants causing severe environmental contamination (Walker et al. 2012). The US Environmental Protection Agency (USEPA) listed HMs as a major category of pollutants under trace inorganic contaminants (Wuana and Okieimen 2011). Conventionally, HMs are defined as those having higher densities or high atomic weight. But now it also includes metallic chemical constituents, metalloids proven to be toxic (Lee et al. 2017). Few metalloids and lighter metals (selenium, arsenic, aluminum) are observed to be harmful in terms of the environment and human health and hence regarded as HMs (Tchounwou et al. 2012; Briffa et al. 2020).

Globally, a steady elevation of atmospheric HM concentrations has been observed over 30 years in few countries. Despite the fact that HMs are naturally found in the Earth's crust, the large increase in their use has led to an impending rise in the amount of metallic components in the environment (Gautam et al. 2016). Naturally, HMs are introduced through rock weathering, volcanic activities, soil erosion, metal corrosion, sediment resuspension, and metal evaporation from water and soil. The prime cause of HM pollution is contributed by anthropogenic activities such as mining activities, smelting, metal-based industries, and metal leaching from sources such as landfills, dumping sites, agricultural fields, livestock manure, etc. (Ali et al. 2021). The use of HM-based pesticides, fertilizers, and insecticides in the agriculture is considered the secondary source of HM pollution (Tchounwou et al. 2012; Gautam et al. 2016; Masindi and Muedi 2018). The widespread utilization in industrial, medical, and agricultural sectors along with others has led to its dispersal in the atmosphere, soil, and water (Wang 2009; Tchounwou et al. 2012; Lenntech 2018); however, HM emission by natural means cannot be overlooked as they contribute to huge quantities of dust comprising of HMs. The principal HMs estimated to have been released from natural resources are chromium (Cr), manganese (Mn), vanadium (V), copper (Cu), molybdenum (Mo), nickel (Ni), lead (Pb), selenium (Se), and zinc (Zn). Over 20% of cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and selenium (Se) in the atmosphere maybe attributed to volcanic activities (Allen et al. 2001). Of the total emissions into the atmosphere, sea salt aerosols contribute almost 10% of it (Allen et al. 2001). Fly ash (FA), released during coal combustion, is reported to contain

HMs. During 2001–2002, India was reported to emit >100 million tons of HM-enriched FA per year owing to the high ash content of coals (>32%) (Smith 2005). Although most of the HMs are natural environmental constituents, its biochemical equilibrium and geochemical processes have been altered by indiscriminate anthropogenic activities owing to the demand for better quality of life with modern conveniences (Briffa et al. 2020).

The contaminants are introduced into the atmosphere through a range of ways, including particles, droplets, and gases, or associated with other particles or droplets. Because they are too small to travel great distances, particles and droplets normally land on the ground after just a small distance (Ali et al. 2021). Particles smaller in size (<10 μm) and density persist for longer durations in the atmosphere and can be relocated over great distances. Air consistency along with vigorous vertical mixing circulation patterns promotes the distribution of pollutants in the troposphere layer. Once entering the air circulation, air pollutants can travel long distances and cause global environmental pollution issues. Soluble particulates react with rain and precipitate onto the water and land (Walker et al. 2012). Except for the metal Hg occurring in gaseous form, other atmospheric HMs of either natural or anthropogenic sources are chiefly associated with particulate matter. Metals of diameter ranging between 0.01 μm and 100 μm are adsorbed by particulate matter. The health impacts and haze episodes linked with atmospheric particle matter (PM) are of major concern to the public and government entities. PM has a high capacity for adsorbing hazardous metals, which can then enter the human body by breathing and cause negative physiological effects (Li et al. 2013). Wet and dry deposition of metal elements adsorbed to air PM can be seen in soils, aquatic bodies, and plant leaves. They may then accumulate in plants or animals as a result of metabolic processes, exposing people through the ingestion of contaminated plants or animals (Li et al. 2013). Sand storms, soil erosion, volcanic activities, and rock weathering are processes through which PMs are released. Meanwhile, burning of fossil fuels, smelting, vehicle exhaust, industrial activities, etc. are anthropogenic activities contributing to the PMs into the atmosphere (Briffa et al. 2020). As a result, a plethora of health implications including cancer and damage to essential organs as well as cardiovascular and pulmonary inflammation and acute respiratory disorders have been recorded mainly among urban populations (Fig. 4.1).

This chapter intends to provide a summary of HM pollution in the atmosphere and its consequences on air quality and the implications for human health. The sources and atmospheric pathway of some common HMs in the environment have been thoroughly discussed, as well as their toxicological impact on human health. The environmental bioaccumulation of hazardous components in human food chains and eventual human body contact are both facilitated by HM-contaminated media. In this chapter, the effects of common HMs on the human body are explored in terms of the amount and duration of exposure. To explore environmentally relevant HMs and their sinks and remobilization processes between air, soil, and water compartments, it is vital to analyze their transports together with fates and behaviors in air-water-soil biota. These concepts would be beneficial for future risk assessment, such as understanding ambient environmental variables; discovering, tracking, and

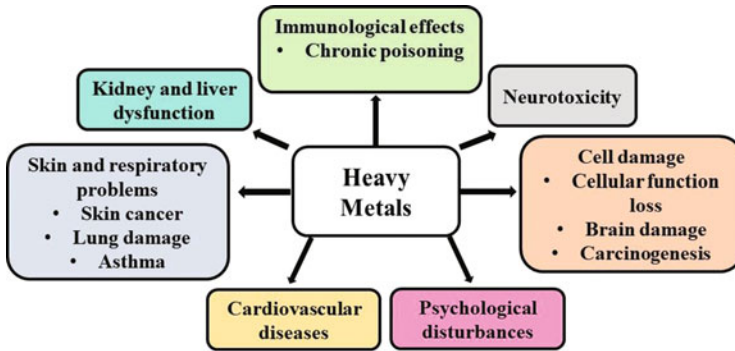


Fig. 4.1 The impact of heavy metals on the human body

analyzing problems that have occurred; and creating and ensuring command and control methods (Cheevaporn 2004).

4.2 Most Common Air Pollutants and Their Sources

Population expansion at a very uncontrollable rate is the chief cause of pollution with the peripheral causes of human activities, energy demands, and industrialization. However, besides this factor, there are several other contributing elements such as the use of biofuel, crop residue burning, biomass combustion, wood combustion, brick kilns, cremation, coal-based power plants, cyclones, forest fires, construction activities, long-range transport of dust, mining, and vehicular emissions (Ali et al. 2021). These activities have led to declining air quality, deteriorating human health, alterations in the meteorological conditions, precipitation rates and patterns, rate of snow melting, and causing acid rains. Moreover, atmospheric pollution along with degrading air quality can bring about ozone depletion, regression of biodiversity, economical loss, water, and land pollution, consequently acting in a comprehensive manner leading to a global change. The most commonly present atmospheric pollutants are Pb, Hg, and Cd; however, As, Mn, Cr, Co, Sb, Be, Se, and Ni are also observed to be present in high concentrations in the atmosphere.

Pb is a persistent contaminant which pollutes water, soils, and sediments by wet and dry deposition. Long-range wind transmission of soil particles, marine aerosol, volcanoes, biogenic materials, and forest fires are all natural sources of Pb. There is no volcanic component in India or its vicinity that can add to lead in the environment. In the mid-1990s, natural fluxes accounted for around 10% of total anthropogenic air emissions (Nriagu 1989). Coal, wood, and petroleum combustion, high-temperature metallurgy, the timber industry, and rubbish burning are all major anthropogenic contributions. Pb levels in the upper continental crust are at 170.5 ppm (Das 2022). As a result, crystal dust could be a major natural contributor of Pb in the atmosphere. In March 2012, Pb out of a strong Middle Eastern dust storm was detected over Delhi, India (Kumar et al. 2016). In India, coal burning is

the most significant anthropogenic source of atmospheric Pb, which has expanded to fulfill the rising energy demand. Other source includes high-temperature enterprises like smelters and gasoline combustion, in addition to coal burning. India's high-temperature vehicle sector is rapidly growing, and the ever-growing fleet of automobiles in the cities is a significant Pb source in the atmosphere (Kumar et al. 2016). Organolead added to gasoline was a substantial source of exposure. Organic Pb was converted to inorganic lead oxide during combustion in car engines and released about completely in that form. This resulted in inorganic Pb exposure, particularly among those who lived in high-traffic regions. People who reside in urban regions have greater β -Pb levels than those who live in rural areas. In the Indian metropolis of Lucknow, Kaul et al. (2003) found 2000–3900 ng/m³ in traffic zones. Residents in the vicinity may be exposed to industrial pollution and recycling processes. Furthermore, resuspension of polluted soils influences exposures due to environmental pollution from past industrial emissions. As a result, Pb exposure is enhanced in proximity to historical or present industrial sources, through inhalation and, probably more critically, consumption (due to children's hand-to-mouth activities). Weathering, chalking, and peeling paint releases environmental exposure to Pb-containing particles; Pb carbonate hydroxide has seen extensive use as a pigment in house paint in several nations. Dust in houses with a Pb-based paint and soil near Pb-emitting enterprises, for instance, can contain extremely high amounts of Pb (WHO/IPCS 1995; CDC 2002).

Hg exists naturally in the environment; however, in recent decades, human activity has profoundly altered its cycle. Volcanic eruptions and ocean discharges are both natural sources of Hg in the environment. Anthropogenic emissions include those from raw materials or fuels, applications in merchandise, and industrial processes. The major source of anthropogenic Hg emissions (37.7%) is artisanal and small-scale gold mining (ASGM), followed by stationary coal combustion (21%). Manufacturing of cement and nonferrous metals both account for 11% of total emissions. Since it was first released into the environment in small amounts, the Hg contained in it today can be transferred into the atmosphere through land, water, and other surfaces (US EPA).

Cd is released into the air by natural and artificial sources. Naturally, the chief sources of Cd in the atmosphere are windborne debris, biogenic emissions, and volcanoes (Nriagu 1989). The major contributor to airborne Cd is smelters. Additional sources of airborne Cd include burning fossil fuels, as well as incineration of municipal waste such as plastics and Ni-Cd batteries (ATSDR 1999). Iron and steel factories are another source of atmospheric Cd emissions. Smelting, soldering, and other high-temperature industrial activities produce Cd oxide as minute particles in the air (fume). When released into the environment, Cd compounds have the potential to bind with respirable airborne particles and travel long distances. Rain or falling from the sky deposits it on the ground below. Cd is rapidly absorbed into the food chain by plants such as green vegetables, root crops, cereals, and grains once it has fallen to the ground (ATSDR 1999).

Cr, a metallic element, is one of 129 priority pollutants identified by the USEPA and one of the 25 hazardous compounds that priority superfund sites have been

found to contain the highest risk to human health. The largest natural emitter of Cr in the environment is continental dust flux. Anthropogenic sources provide more than 70% of Cr to the atmosphere, primarily from metal industry emissions and fuel combustion. Ferrochrome production, ore processing, chemical and refractory treatment, cement-making facilities, vehicle brake linings, and catalytic converters, leather tanneries, and chrome pigments are the most common sources of high atmospheric Cr exposure. The annual emissions of Cr from coal and oil burning are projected to be 1723 metric tons (ATSDR 1999).

As is a naturally occurring element that cycles through water, land, air, and living systems. High-temperature events such as coal-fired energy plants, burning vegetation, and volcanism release As into the atmosphere. As is liberated as highly soluble oxides as a result of combustion processes. As is also released by spontaneous biomethylation and reduction in low temperature to arsines. As, commonly discharged as As_2O_3 , is mostly adsorbed onto a particulate matter. Arsines are released by microbial sources in soils or sediments which are oxidized in the air and reverted to nonvolatile forms, which are re-deposited on the soil. As a result of biogenic processes, gaseous alkyl As compounds are emitted from soil that has been treated with inorganic As compounds. Humans are predicted to breathe 40–90 ng of As per day, as recommended by the USEPA (Chung et al. 2014).

Mn is a necessary component of metabolic processes, but excessive quantities in the body can be hazardous, resulting in substantial neurologic and mental damage (Ranucci and Iorio 2019). In the environment, the occurrence of natural compounds of Mn is being steadily replaced by enrichment due to human activity. Mn emissions in the atmosphere are estimated to be 38.27 kt yr^{-1} by Livett (1992), with the biggest contributions coming from ferrous metal smelting and oil combustion. Mining, iron/steel manufacturing, ferro-/silico-Mn alloy and dry alkaline battery production, and welding are the main sources of Mn exposure. Low levels of Mn exposure in the environment are typically attributed to industrial sources, agricultural use, and the addition of Mn compounds to fuel. Since the addition of methylcyclopentadienyl Mn tricarbonyl (MMT) to unleaded gasoline, an increase in the atmospheric Mn content has been anticipated. Mn exists in atmospheric particles primarily as varying oxides that readily react with SO_2 and NO_2 and become water-soluble (Lucchini et al. 2014). On average, approximately 20 ng/m^3 Mn is reported in the air as per the ATSDR toxicological profile.

Sb ores are found in the crust of the Earth naturally. Sb oxides can be released into the environment by volcanoes. Anthropogenically, Sb oxides are a derivative of smelting lead and other metals, as well as coal-based power plants. Being a common component of coal and petroleum, emissions from car exhaust also contribute to Sb release. Refuse incinerators, minor industrial operations such as lead casting, and fossil fuel burning, for example, for home heating also cause emissions to air and land (NPI). Sb concentrations in ambient air range from $>1 \text{ ng/m}^3$ to around 170 ng/m^3 according to the EPA's TTN ATW webpage; it may be observed at levels as high as 1000 ng/m^3 close to companies transforming Sb ores into metals or manufacture Sb oxide.

Pure Be, a hard gray metal, rarely exists naturally but is found in some types of rocks, coal and oil, soil, and volcanic dust as a chemical component. It can also be found in Be fluoride, Be chloride, Be sulfate, Be oxide, and Be phosphate, among other compounds. Be levels in the air next to the Be processing sector in Mumbai, India, were detected at 0.42–0.48 ng m⁻³ ($N = 397$) (Thorat et al. 2001).

Ni is the fifth most common metal. The Earth's surface and core are both rich in this silvery-white, lustrous metal. Wind-blown dust, generated from rock weathering and soils, forest fires, and volcanic activity are all natural producers of environmental Ni. Ni is also released due to the combustion of coal, diesel oil, and fuel oil, as well as the incineration of trash and sewage. The presence of Ni compounds in the air is primarily due to the combustion of fossil fuels (Genchi et al. 2020). Each cigarette has been observed to contain 1.1 to 3.1 g of Ni and may be available as Ni carbonyl in tobacco smoke, which is particularly dangerous to human health (Cempel and Nikel 2006).

Co exists as cobaltite, skutterudite, erythrite, spherocobaltite, and heterogeneity and can be found in both sedimentary and igneous rocks in excess. Co is found in 5–30% of cemented carbide. Co-leaching is caused by cement plants and carbide tool grinding operations (Lu et al. 2016). E-waste processing industries have also been discovered to leak Co at amounts exceeding the permitted limit (Lim and Schoenung 2010). Fine Co polishing discs are also utilized in diamond polishing. It also can generate Co dust (Leysens et al. 2017). Co is also used as a siccative in the pigment and paint industries to speed up the drying process (Christensen and Poulsen 1994). Bottom ash from incinerators contains Co, which leaches into the soil and groundwater.

Se is a chalcogen element found in rocks and soil and is a widely dispersed element on the Earth's surface. Se is sometimes referred to as elemental Se or Se dust when existing in its purest form (Handa et al. 2016). Forest fires, volcanic activity, and soil erosion are all connected to Se origin. Se is also produced by human activities including the burning of trash, tires, paper, and other fossil fuels. The chief sources of atmospheric Se compounds are coal and oil combustion. According to their behavior in the atmosphere, three types of Se compounds can be distinguished: volatile organic molecules (DMSe, DMDSe, and methaneselenol), volatile inorganic compounds (selenium dioxide), and elemental Se attached to ashes or particles. In the atmosphere, dimethyl selenide is stable, whereas hydrogen selenide and Se dioxide are both unstable. Se and water are formed when hydrogen selenide is oxidized. In moist conditions, Se dioxide is converted to selenious acid (Mehdi et al. 2013).

Atmospheric particulate matter (PM) is of major concern for the public and government entities concerning the associated health impacts and haze events. Hazardous metals that can eventually enter the human body by breathing and create physiological issues have a high ability to adsorb in PM. PM can be released into the atmosphere directly or produced indirectly from gaseous precursors, primarily sulfur dioxide, nitrogen oxides, ammonia, and non-methane volatile organic compounds (Geiger and Cooper 2010).

4.3 Exposure Pathways of Atmospheric Heavy Metals

Inhalation and cutaneous contact are the two most common routes for metal intake in humans, both of which use air as the principal medium of interaction. The assessment of exposure is based on ambient and anthropogenic concentrations as well as numerous exposure routes (Geiger and Cooper 2010). People can risk their health by being exposed to dangerous air pollution in a variety of ways, including:

- a. Inhaling contaminated air; consuming contaminated foods, such as fish sourced from polluted waters; meat, milk, or eggs from animals that consumed contaminated vegetation; and fruits and vegetables produced in contaminated soil that has been sprayed with air toxics.
- b. Consuming polluted drinking water or soil contaminated by harmful air pollutants. Because they frequently swallow the dirt on their hands or the items they put in their mouths, young children are particularly vulnerable.
- c. Contacting polluted dirt, dust, or water with one's skin (during recreational use of contaminated water bodies).

Air plays a role in many indirect pathways, including the deposition of metals to surface dust and intake through ingestion, inhalation, or dermal contact; deposition of metals to surface water and sediment and intake through ingestion and dermal contact; and absorption of deposited metals into aquatic and/or terrestrial biota, as well as entry into the food chain and ingestion. Although inhalation of surface dust is the primary contributor to human health risk in most cases where airborne elements have culminated in environmental contamination, this is not always the case. Inhaled metals have a substantially higher bioavailability than other forms of ingestion (Geiger and Cooper 2010). Even while inhaled doses are equivalent to intakes through other ways, this can result in extremely large internal dosages. Cigarette smoking, for example, contributes significantly to the bioaccumulation of Cd (Newman et al. 2004).

Due to differences in airway geometry and inflow velocities, which cause larger absorbed particulate deposition fractions in young children and infants than those in adults at the same exposure levels, infants and children are more vulnerable to airborne metal particles. Furthermore, studies demonstrate that particle pollution can limit children's lung function growth (C. EPA 2004).

4.4 Assessment of Heavy Metals in the Atmosphere

The current status of concentrations of HMs is crucial to present a good overview of ambient air quality in terms of heavy metal content in ambient air. Between 2000 and 2004, Fang et al. (2005) examined the atmospheric metallic elements throughout Asia. Fe was discovered to be the most prevalent element in Asian countries, varying in the value range from 165,000 to 265,500 ng m⁻³. A significant concentration of Zn linked with total suspended particulate matter (TSP) was discovered in Taichung,

Taiwan, according to this study (1060 ng m^{-3}). Similar to TSP, a high quantity of Pb ($820\text{--}1060 \text{ ng m}^{-3}$), Cu ($370\text{--}1550 \text{ ng m}^{-3}$), and Mn ($850\text{--}1470 \text{ ng m}^{-3}$) was found in Mumbai (India). At Sapporo and Tokyo, Ni ($3.81\text{--}5.63 \text{ ng m}^{-3}$) and Cr ($2.61\text{--}6.09 \text{ ng m}^{-3}$) associated with TSP were measured.

Wu et al. (2007) examined the trace metal contaminants related to atmospheric fine particulate matter of Asian countries from 1995 to 2005. According to this study, the Asian countries with the greatest mean concentrations of HMs connected with $\text{PM}_{2.5}$ were Mg (126.85 ng m^{-3}) > Fe (126.99 ng m^{-3}) > Zn (126.99 ng m^{-3}) (93.48 ng m^{-3}). Vehicle exhaust was the largest source of components such as Cr, Pb, Cu, Zn, and Cd in ambient particulate matter in Asian countries, according to the researchers. The primary source of elements like Zn and Pb is incineration, and the primary sources of Cr and Ni are coal combustion and industrial oil combustion, respectively. In the last 25 years, the toxicity of fine PM ($1\text{--}2.5 \mu\text{m}$) and ultrafine PM ($0.1\text{--}1 \mu\text{m}$) has been found to significantly increase human fatalities and morbidity (Geiger and Cooper 2010). However, emerging research during the last decade has indicated the toxicity of metallic constituents might be more hazardous as compared to other components of PM (Konkel 2009). The growing belief was that HMs adsorbing on PM is critical to its toxicity and detrimental health consequences. PM has been associated with a variety of illnesses, including cardiovascular and respiratory illnesses, as well as lung cancer (Li et al. 2013). Even at low levels, metals associated with PM present in ambient air have shown significant adverse health effects. Bushfires in Singapore resulted in substantial increases in Zn, Fe, and Cu concentrations. As a result, the number of patients seeking medical treatment for respiratory problems increased by 25% and the number of asthma cases increased by 29% (Karthikeyan et al. 2006).

The behavior of the PM in the mammalian respiratory system is determined by its aerodynamic properties and composition (Pendias and Mukherjee 2007). Studies have revealed that finer PM is more soluble and has high toxicity causing oxidative stress and inflammation (Sangani et al. 2010). In India's residential regions, the yearly mean concentration of PM_{10} (a primary source of HMs in the atmosphere) is three times greater than WHO standards. The standard yearly and 24-hour mean Pb values, according to India's National Ambient Air Quality Standards (NAAQS), were 500 ng/m^3 and 1000 ng/m^3 , respectively. As and Ni had normal annual mean concentrations of 6 and 20 ng/m^3 , respectively (The Gazette of India 2009). The ambient concentrations of As in residential neighborhoods of Hyderabad during the fireworks event were measured and reported by Kulshrestha et al. (2004) to be 25 ng/m^3 , which is greater than the NAAQ guidelines. From March 2006 to May 2008, Kulshrestha et al. (2009) examined ambient Pb concentrations related to PM_{10} and $\text{PM}_{2.5}$ in urban and rural areas of Agra, finding two times higher Pb concentrations than the NAAQ requirements. In aerosols throughout the Delhi-Hyderabad-Delhi Road corridor, Singh et al. (2010) observed higher amounts of Zn, Mn, Cd, and Pb linked with PM_{10} in urban and semi-urban areas than in rural areas. The air quality in India is deteriorating as a result of urbanization and industrialization. HM concentrations in India are equivalent to those found in China and Pakistan, but greater than those reported in other developed Asian countries such as South Korea,

Japan, and Hong Kong. In China and India, fireworks during festivals raise the particulate matter and HM levels in the air. A major global risk factor is prolonged exposure to air pollution (Chen et al. 2022), arising from energy production, traffic, and industries which is a major consequence of the present industrial state and the increasing demand for a better quality of life with modern conveniences. Regulatory bodies at central, state, and local levels were set up to monitor and assess the air quality and categorize it as either safe or unsafe for breathing. The regulatory bodies are responsible for asserting standards or levels or goals for air quality (Geiger and Cooper 2010).

According to estimates from the World Health Organization, around 800,000 early deaths are brought on by urban air pollution which also reduces the life expectancy of 4.6 million people each year across the world. Developing nations are especially susceptible to rising amounts of airborne metals in the ambient atmosphere because they lack the regulatory infrastructure necessary to properly monitor and manage air toxins. PM pollution is responsible for 22,000 to 52,000 early deaths annually in the United States and 200,000 early deaths in Europe (Mokdad et al. 2004). Globally, 4–8% of premature deaths are owed to exposure to suspended PM, primarily in the indoor and ambient environment due to fine PM exposure. Country or state borders do not limit the emissions by the industries and other mobile sources. As per Health Effects Institute in Boston, Massachusetts, developing Asian nations account for two-thirds of the 800,000 early deaths brought on by urban air pollution (HEI 2004). Some of these nations, like some African nations, do not have sufficient industrial activity to pose concerns to human health, but others, like Mexico and China, have industrialization-related air toxics at levels considerably above what would be considered “safe” in more controlled systems (Geiger and Cooper 2010).

4.4.1 Metals in Particulate Matter

The concentration of HMs in particulate matter, particularly tiny particles such as PM_{2.5}, can endanger human health. The burning of garbage, high-temperature industrial processes, and the combustion of fossil fuels and timber all emit trace metals into the atmosphere. Volcanoes, wind erosion, forest fires, oceans, and other natural events are the primary sources of natural emissions (Nordberg et al. 2007). The major sources of Be, Co, Hg, molybdenum, Ni, Sb, Se, tin, and vanadium is specifically the burning of fossil fuels. Burning fossil fuels also adds to the emission of As, Cr, copper, Mn, and zinc by humans. A significant amount of As, Cd, Co, Ni, and zinc are also released during industrial metallurgical processes. Pb, Cu, Zn, Ni, and Cd were once present in varying degrees in gasoline exhaust fumes. Zn emission and tire rubber abrasion are connected (Councell et al. 2004) (Table 4.1).

The size of airborne particles determines the possibility for inflammatory inflammation, oxidative damage, and other biological impacts, according to several different groups of researchers (Costa and Dreher 1997; Ghio et al. 2002; Lippmann et al. 2006; Sangani et al. 2010). The deposited fraction of inhaled particles in distinct

Table 4.1 Industrial limits ($\mu\text{g m}^{-3}$) for hazardous metals in air and their adverse health effects

Metal	NIOSH REL (10 h TWA) ($\mu\text{g}/\text{m}^3$)	OSHA PEL (8 h TWA) ($\mu\text{g}/\text{m}^3$)	OSHA limit for work place air ($\mu\text{g}/\text{m}^3$)	Toxic effects
Sb	500	500		Affects skin and eyes, inflammation of lungs, chronic bronchitis, chronic emphysema, tuberculosis, cardiovascular effects, edema, and hemorrhage
Al				Dementia, central nervous system damage, kidney and liver dysfunction, colitis, lung damage, pulmonary fibrosis, hypoparathyroidism
Cd	N.E.	0.005	5	Kidney damage, prostate dysfunction, bone diseases and cancer, kidney dysfunction and proteinuria, lung cancer, osteoporosis
Cr	0.5	1	0.5–1000	Breathing problems, such as asthma, cough, shortness of breath, chronic poisoning, dermatitis, eczema, gingivitis, bronchitis, liver and kidney disease, sinusitis, pneumonia, lung cancer
Cr (III)	0.5	0.5		
Cr (VI)	0.001	0.005		
Co	0.05	0.1		Skin and respiratory problems, acute effects such as congestion, edema, lung hemorrhage, ventilator function reduction. Chronic inhalation may cause asthma, respiratory irritation, pneumonia, fibrosis, reduced lung functions, cardiac effects, nausea and vomiting, diarrhea, liver disorders
Cu	1	1		Liver cirrhosis, chronic anemia, brain and kidney dysfunction, stomach and intestine infection
As	2	10	10	Skin cancer and marked problems with circulatory system, developmental abnormalities, neurobehavioral sicknesses, cardiovascular diseases and hearing sickness, anemia, leukopenia, eosinophilia, and carcinoma. A sensation of “pins and needles” in hands and feet, darkening of the skin and the appearance of small “corns or warts” on the palms, feet, and torso, lung cancer, liver and kidney damage
Be	0.5	2		Inflammation of lungs, acute pneumonitis, berylliosis, shortness of breath, fatigue, immunological effects
Pb	50	50	50	Anemia, brain and kidney damage, affects the neurological system, impaired

(continued)

Table 4.1 (continued)

Metal	NIOSH REL (10 h TWA) ($\mu\text{g}/\text{m}^3$)	OSHA PEL (8 h TWA) ($\mu\text{g}/\text{m}^3$)	OSHA limit for work place air ($\mu\text{g}/\text{m}^3$)	Toxic effects
				cognitive and motor function, miscarriage, infertility, carcinogen
Mn	1000	5000		Central nervous system dysfunction, manganism, weakness, lethargy, affects lungs
Hg	0.1	100	100 for organic Hg, 50 for metallic Hg	Tumor, memory loss, restlessness, depression, psychological disturbances, fatigue, insomnia, lung damage, kidney failures, death of fetus, gastrointestinal issues, increase in blood pressure
Ni	15	1000		Skin allergy, cancer of lungs, nose, sinuses, throat, immunotoxic, neurotoxic, genotoxic, loss of fertility
Se	200	200	200	Nausea, diarrhea, stomach pains, bronchitis, respiratory infection, selenosis, hepatotoxicity
V	50	50		Throat, nose, and eye irritations, nose bleeding, dizziness, headaches, nausea, impairment to the nervous system, liver and kidney hemorrhage, paralyses and behavioral changes, cardiac diseases
Ag	10	10	10	Argyria, a blue-gray discoloration of the skin and other body tissues, breathing problems, lung and throat irritation, stomach aches, mild allergic reactions

NIOSH = National Institute for Occupational Safety and Health; OSHA = Occupational Safety and Health Administration; REL = recommended exposure limit; PEL = permissible exposure limit; TWA = time-weighted average

parts of the respiratory tract is determined by the particle size distribution of an aerosol (Oller and Oberdorster 2010). PM is a complex mixture of extremely small particles and liquid droplets that include acids (such as nitrates and sulfates), organic compounds, metals, and soil or dust particles, among other things. The EPA is particularly interested in particles having a size of 10 μm or smaller since they enter the lungs through the nose and throat. If inhaled, these particles can damage the heart and lungs, travel throughout the body, accumulate in organs, pierce cell membranes, and result in serious health issues (Geiger and Cooper 2010). “Inhalable coarse particles,” similar to that found near highways and dusty industries, are $\geq 2.5 \mu\text{m}$ in diameter and $< 10 \mu\text{m}$ in diameter, according to the EPA. Fine particles, like those observed in smoke and haze, have a diameter of 2.5 μm or less. These particles may be released directly from events like forest fires or may develop in the atmosphere as a result of the reaction of gases produced by power plants, industries, and automobiles (Geiger and Cooper 2010).

As detailed by Nieboer et al. (2005), these particles can be further classified in terms of significant health impacts for specific regions:

- a. The proportion of cumulative airborne particles entering the body through the mouth and/or nose during respiration is known as the “inhalable aerosol fraction.” This fraction, which corresponds to particles with an aerodynamic equivalent diameter (dae) more than 100 m, is important for health impacts in the respiratory system, such as lung cancer, bronchitis, nasal irritation, and rhinitis. This proportion is also important in terms of systemic impacts.
- b. The “thoracic aerosol fraction” [dae < 30 m] is a subfraction of the inhalable fraction that is essential for the treatment of lung cancer, bronchitis, and asthma because it contains particles that can enter the tracheo-alveolar region of the lung.
- c. The “respirable aerosol fraction” (also known as the “alveolar fraction”) is a subfraction of inhaled particles [dae < 10 m] that permeates into the alveolar surface of the lung and is crucial in the development of chronic diseases including pneumoconiosis and emphysema.

4.4.2 Characteristics of Fine Particulate Matter

The World Health Organization estimates that 2.4 million people each year die as a result of air pollution, primarily from small particles (WHO 2002). According to recent studies on human health, free radicals similar to those found in cigarettes are also common in airborne fine particles and may cause many of the same potentially fatal diseases (Dollemore 2008).

Utsunomiya et al. (2004) postulated homogeneously dispersed poisonous trace metals represent a concern to human health and the environment as pollutants in coarser, insoluble particles but the dangers are greatest if they are present as primary components in individual, trace metal, microscopic particles. The majority of studies generally indicate that the toxicity caused by oxidative stress and inflammatory processes increases with decreasing particle size and solubility (Valavandis et al. 2008). Metals were found to be a prominent source of cellular oxidant production and associated health consequences in research of PM_{2.5} (Maciejczyk et al. 2010). Metal size distribution studies demonstrate that the majority of harmful metals collect in the tiniest particles (PM_{2.5} or less) (Khaiwal et al. 2008). This small fraction may penetrate deeper into the respiratory tract, settling mostly in the alveolar region of the lungs, where trace element absorption effectiveness ranges from 60% to 80% (Pope and Dockery 2006). When a metallic ion comes into touch with lung tissue/cells, they are released into the biological system (Midander et al. 2007). The maximal residence time (100 days) for fine and ultrafine particulate matter in the atmosphere allows for a broad geographic dispersion (Utsunomiya et al. 2004). Ultrafine particles are considered to be more soluble than larger particles of the similar composition due to the high surface-to-volume ratio for small sizes (Navrotsky 2001). According to recent studies, the metal fraction of fine and ultrafine PM is extremely harmful and is the main cause of poor human health

(Magari et al. 2002). Additionally, these particles influence climate change and can be carried by strong winds over long distances (WHO 2007). To fully understand these findings' possible health effects, chemical characterization of the fine and ultrafine fractions of airborne particles must be prioritized (Khawaiwal et al. 2008).

4.5 Public Health Concern

Industrialization, modern urbanization, and rapid economic development have all resulted from the increased use of HMs in industrial and agricultural activities around the world. These practices potentially pollute water, air, and soils with harmful HMs. HM-contaminated media lead to environmental bioaccumulation of toxic elements in food chains, ultimately impacting the human body. HM has a range of health concerns in humans, determined by the amount and duration of exposure (Ali et al. 2021).

4.5.1 Health Implications

The toxicity of an HM relies on the entry pathway of the metal, its entry rate, the distribution in tissue, the concentration retained, and the excretion rate. Inhibition of enzyme activities and protein synthesis, altering the functions of nucleic acid, and altering the cell membrane permeability are toxicity mechanisms induced by HMs (Bernardo 2021).

Cell organelles such as mitochondria, lysosomes, and nuclei along with cell membrane and enzymes are affected by HMs. The metal ions are associated with DNA and nuclear proteins leading to site-specific DNA damage (Valko et al. 2005; Tchounwou et al. 2012). The damages may be direct or indirect. Direct damages include structural alterations in the biomolecules due to association with the metal ions. Lipid peroxidation, DNA damage, altered sulfhydryl homeostasis, and free radical production are all effects of HM toxicity. The formation of reactive oxygen and nitrogen species containing hydroxyl and superoxide radicals, nitric oxide, hydrogen peroxide, and more endogenous oxidants is considered indirect damage (Valko et al. 2005). Copper, Cr, iron, Ni, and Cd have been observed to produce free radicals. Iron, copper, Cr, and Co follow Fenton reactions linked to peroxisomes, mitochondria, and microsomes (Valko et al. 2005). The metal-mediated free radicals result in DNA base mutation showing a vital linkage between carcinogenesis and oxidative stress. As, Cd, and Ni have been observed to inhibit DNA repair mechanisms (Valko et al. 2005; Briffa et al. 2020).

Recent studies have found that some metals can harm the nervous system and olfactory system. The neurological system and the outer world are directly connected by the olfactory system (Aschner et al. 2005). Foreign substances can reach the brain through the olfactory (nasal) neuron (Bondier et al. 2008). Metals that can travel through the olfactory nerve include aluminum, Cd, Co, Hg, Mn, Ni, and zinc.

4.5.2 Hazardous Air Pollutants (HAP)

The EPA's Health Effects Notebook for Hazardous Air Pollutants lists 11 distinct metals (EPA, Health Effects Notebook for HAPs 2010). HAPs, commonly referred to as harmful pollutants or air toxins, are contaminants that induce or may increase the risk of cancer as well as other serious health effects including birth defects or reproductive issues, as well as detrimental effects on the environment and the ecosystem. The information presented here is meant to serve as a basic overview rather than a full reference for metals' health impacts. The data for the Air Toxics Website (ATW) (EPA, Technology Transfer Network 2010), which incorporate information from the Agency for Toxic Substances and Disease Registry (ATSDR 1999), the Integrated Risk Information System (IRIS 2010), and the EPA, as well as recent air research, are presented in the following subsections. Additional sources of information on health effects include the California Office of Environmental Health Hazard Assessment, the Hazardous Substances Data Bank (HSDB 2010), and the American Conference of Governmental Industrial Hygienists (ACGIH 2010; OEHHA 2008).

4.5.2.1 Antimony (Sb)

Inhalation of Sb can cause skin and eye irritation, while ingestion might cause gastrointestinal problems. High acute exposure to Sb has caused respiratory consequences in animals, including a significant drop in ventilatory function, congestion, edema, and bleeding, in addition to liver and cardiovascular damage. Respiratory issues such as lung inflammation, chronic bronchitis, and chronic emphysema can be brought on by prolonged inhalation. Respiratory side effects include pleural adhesions, irritation, chronic bronchitis, chronic emphysema, latent tuberculosis, Sb pneumoconiosis (lung inflammation), and chronic bronchitis. There have also been reports of cardiovascular problems. Sb inhalation has been related to lung malignancies in animals, although no definitive link between cancer and Sb has been discovered in people. Sb has not been categorized as carcinogenic by the EPA.

4.5.2.2 Arsenic (As)

Inorganic As is most commonly absorbed through food, with smaller quantities absorbed through drinking water and breathing. Inhalation can happen in metal smelters and while burning wood that has been processed with an As preservative. Arsine poisoning is caused by inhaling it. As has no odor or flavor. Acute inorganic As inhalation and ingestion can cause gastrointestinal consequences (nausea, diarrhea, abdominal pain) as well as central and peripheral nervous system diseases. Acute inorganic As poisoning can end in death. Arsine is exceedingly poisonous, and exposure can cause abdominal discomfort, vomiting, and headaches within a few hours of exposure. Acute arsine poisoning might also result in mortality. Reduced production of red and white blood cells, an unsteady heartbeat, blood vessel damage, and a "pins and needles" feeling in the hands and feet are all symptoms of lower exposure levels. Skin and mucous membrane inflammation can occur after inhaling inorganic As. Long-term oral consumption can result in

gastrointestinal problems, anemia, peripheral neuropathy, liver or renal damage, hyperpigmentation, and skin lesions. Reduced exposure over time can discolor the skin and create little corns or warts on the palms, soles, and torso. A kind of skin cancer and bladder, liver, and lung cancer have all been linked to oral exposure to inorganic As. Women who work in or live close to metal smelters may experience more spontaneous abortions than the general population, and their offspring may be born with lower weights. Inhalation investigations on humans have found that inorganic As exposure is highly linked to lung cancer. The EPA classifies inorganic As as a Group A human carcinogen, with the potential to cause cancer of the skin, lungs, liver, and bladder (ATSDR).

4.5.2.3 Beryllium (Be)

Be is most commonly found in or near facilities that mine, process, or convert it into alloys and chemicals. People can also become exposed through the inhalation of Be dust or fumes from the burning of coal, fuel oil, or tobacco. Be can also be consumed orally and is found in foods like fruits, vegetables, water, and soil.

During the 1980s, the average Be content in the air in the United States was 0.03 ng/m^3 . Between 1977 and 1981, ambient values in 50 cities ranged from 0.1 to 0.4 ng/m^3 . High levels of Be can cause acute pneumonitis or lung inflammation when inhaled for a brief period (reddening and swelling of the lungs). After exposure, symptoms may be reversible. Be compounds have been demonstrated to exhibit a wide spectrum of acute toxicity in animal tests, varying from mild to extreme acute toxicity when administered orally. Prolonged Be exposure can cause chronic Be illness (berylliosis), which causes noncancerous granulomatous lesions in the lungs. Chronic Be disease symptoms include mucous membrane irritation, decreased lung function, shortness of breath, malaise, fatigue, anorexia, dyspnea, and weight loss. In humans and animals, chronic inhalation exposure has had immunological consequences. Chronic pneumonitis, conjunctivitis, and skin allergies are some of other long-term consequences. The inhalation of Be is thought to increase the risk of developing lung cancer in humans, and animal studies have also linked the inhalation of Be to the disease. Be is a Group B1 probable human carcinogen according to the EPA.

4.5.2.4 Cadmium (Cd)

Based on the maximum concentrations of Cd detected in rural, urban, and industrialized sectors, the quantity of Cd inhaled does not surpass 0.04 , 0.2 , and $0.4 \text{ } \mu\text{g/day}$, respectively, assuming a daily inhalation of 20 m^3 . Inhalation exposure is modest in the general population, but in locations with polluted soils, particularly where roadways have been coated with leftovers from nonferrous metal processing, home dust is a potentially substantial and persistent source of Cd exposure (e.g., zinc ashes or sintels as oven sludge). The cigarette is a potential source of Cd that is greater than that found in food. Cd levels in cigarettes range from 1 to $2 \text{ } \mu\text{g}$ per cigarette. Approximately 10% of this is inhaled during the smoking process. Consequently, a person who smokes 20 cigarettes a day will ingest about $1 \text{ } \mu\text{g}$ of Cd (Järup et al. 1998). According to Erzen and Kragelj (2006), light-to-moderate smokers

(>20 cigarettes per day) had a median blood Cd (B-Cd) concentration of 0.5 µg/L, heavy smokers (<20 cigarettes per day) had 1.5 µg/L, and nonsmokers had none.

Kidney and bone damage and cancer are important health endpoints. In Sweden, 820 women aged 53–64 years were studied to see if there was a link between Cd exposure and tubular and glomerular function. Increased B-Cd and U-Cd levels of 0.38 µg/l (median) and 0.52 µg/l (0.67 g/g creatinine), respectively, were associated with higher amounts of human complex-forming protein and N-acetyl-d-glucosaminidase in urine. The correlations persisted even at modest intake doses in women who never smoked. Inhalation exposure in work contexts has also been linked to an elevated risk of lung cancer. The inputs from transboundary air pollution and the usage of mineral and organic fertilizers in Europe are reasonably similar each year in Europe. They all continue to add to the relatively considerable Cd accumulations in the topsoil that already exist.

Cd exposure has been linked to prenatal deformities and other developmental problems in animals, but there is no solid evidence in humans. Cd toxicity from mining in Toyama Prefecture, Japan, causes itai-itai sickness. Cd toxicity resulted in bone softening (brittleness) and kidney failure. Cd is designated as a Group B1 probable human carcinogen by the Environmental Protection Agency.

4.5.2.5 Chromium (Cr)

With an average air level of 3 ng/m³ observed in 13 cities in the United States, the average daily intake of Cr from air is between 200 and 400 ng (AIRS locations) (Chen and Lippmann 2009).

People who reside near Cr waste disposal facilities or Cr production and processing companies are more susceptible to high concentrations of Cr than the general population. Cr (VI) is far more hazardous than Cr (III), causing abdominal pain, vomiting, and hemorrhage in both inhalation and ingestion. Shortness of breath, coughing, wheezing, and other respiratory symptoms like asthma, nasal irritation, and discomfort are all side effects of Cr (VI) inhalation. It can result in pneumonia in the respiratory system, bronchitis, pulmonary dysfunction, and septal perforations and ulcerations. Cr exposure may also affect the liver, kidneys, and gastrointestinal and immunological systems, as well as the blood. Cr (VI) exposure can lead to difficulties throughout pregnancy and labor. Inhaled Cr (VI) is associated with an elevated risk of lung cancer, and Cr (VI) has been demonstrated to produce lung tumors in animal experiments. The Environmental Protection Agency has classified Cr (VI) as a Group A recognized human carcinogen when inhaled.

4.5.2.6 Cobalt (Co)

Respiratory consequences of Co inhalation include a considerable reduction in ventilatory function, lung congestion, edema, bleeding, wheezing, pneumonia, respiratory irritation, asthma, and fibrosis. Chronic exposure can have negative effects on the heart, the liver, the conjunctiva, and the immune system, including the development of Co sensitization. Inhalation exposure to Co has been linked to respiratory, cardiovascular, and neurological effects, as well as lower body weight, thymus necrosis, and blood, liver, and kidney consequences in animals.

4.5.2.7 Lead (Pb)

Pb is hazardous even in small amounts and elevated blood lead can result in fatalities in children. Pb poisoning can cause brain damage, renal damage, and gastrointestinal damage in people who are exposed to it even for a short time. Over time, Pb poisoning can also affect the kidneys, central nervous system, blood, blood pressure, and vitamin D metabolism. Workers have observed neurological problems, as well as delayed nerve transmission in the peripheral nervous system in adults. Chronic Pb poisoning in children can result in IQ loss, slower cognitive development, stunted growth, loss of hearing, and other developmental problems. Possible negative effects of Pb exposure include decreased sperm count, accidental miscarriages, low birth weight, and sluggish postnatal neurobehavioral development. Pb is designated as a Group B2 probable human carcinogen by the EPA.

4.5.2.8 Mercury (Hg)

The lungs collect about 80% of Hg₀ vapor that is inhaled, and this substance is swiftly transported to the kidneys and brain, among other parts of the body. It easily passes through the blood-brain barrier and the placental barrier. The presence of elemental Hg vapors in pregnant women's blood can be transferred onto the growing fetus and deposited there (Geiger and Cooper 2010).

The majority of Hg₀ accumulates in the kidneys, and to a limited extent in the brain, where it is easily transformed to an inorganic form. When exposed to Hg₀, higher Hg is deposited within the brain than when exposed to inorganic Hg compounds. Hg₀'s half-life in the body is expected to be around 60 days (WHO 2003). Acute poisoning from Hg vapor at increased concentrations (higher than 1000 g/m³) for a limited time produces symptoms of lung injury such as extreme airway irritation, pneumonitis, and pulmonary edema. It can harm the brain, nerves, kidneys, and lungs, resulting in coma and/or death in severe cases. Chest discomfort, dyspnea, coughing, hemoptysis, and pulmonary function impairment were all symptoms of the injury among workers chronically exposed to Hg vapor for 4–8 hours (McFarland and Reigel 1978). After prolonged exposure to low amounts of Hg vapor (50–100 g/m³), adverse effects on the kidneys, thyroid, and central nervous system might develop over time and manifest subtly. It's tough to tell the difference between Hg toxicity symptoms and those of other prevalent disorders. Tremors, muscle weakness, melancholy, behavioral modifications, and short-term memory loss are among the symptoms in adults, as are skin rashes, including redness and itching. In children, peeling of the hands and feet is common.

4.5.2.9 Manganese (Mn)

Health consequences of Mn are now being studied by scientists. Side effects of inhalation have been observed in several animal investigations. Based on short-term rat experiments, Mn is judged to have moderate acute toxicity. Mn poisoning affects the central nervous system in a number of ways, affecting functions like eye-hand coordination, hand steadiness, and visual reaction time. Inhalation exposure might have an impact on the respiratory system. When exposed to high quantities of manganese for an extended period of time, manganism, a disease that starts with

feelings of weakness and lethargy, tremors, a mask-like face, and psychological issues, can progress to impotence and loss of libido (Geiger and Cooper 2010).

4.5.2.10 Nickel (Ni)

The lungs and kidneys were damaged in an instance of short-term inhalation exposure to a high quantity of Ni. Contamination of drinking water may cause neurological implications as well as gastrointestinal problems (such as nausea, vomiting, and diarrhea). Exposure to Ni carbonyl can lead to pulmonary fibrosis and renal edema. According to recent studies, Ni can, at ambient levels, cause abrupt changes in heart rate and have other negative effects on health, in part because it has the capacity to create reactive oxygen species (ROS) (Zelikoff et al. 2002).

Ni dermatitis, which causes itching in the fingers, hands, and forearms, can be caused by long-term skin contact. Ni refinery employees exposed to Ni refinery dust have been related to an elevated incidence of lung and nasal malignancies as a result of inhalation exposure (Geiger and Cooper 2010). The EPA classifies Ni refinery dust and nickel subsulfide as Group A human carcinogens, while nickel carbonyl is a Group B2 probable human carcinogen.

4.5.2.11 Selenium (Se)

Acute inhalation exposure to Se compounds such as Se dioxide and hydrogen selenide causes respiratory consequences in humans. Inhaling elemental Se dust for a short duration can induce irritation of the nose and throat mucous membranes, nosebleeds, bronchial spasms, dyspnea, bronchitis, and chemical pneumonia. Oral exposure to hydrogen selenide was found to be extremely hazardous during animal testing. High Se levels taken in over time can result in a variety of side effects, including hair loss, severe tooth decay, a strong garlic odor in the breath and urine, mental weariness, and listlessness (Geiger and Cooper 2010).

The EPA follows these processes to evaluate the remaining danger posed by HAPs:

- Evaluation of the degree of public exposure
- Evaluation of the nature and impact of negative consequences
- Dose-response assessment
- Characterizing overall risk

Thus, so far, there are currently no residual risk requirements involving sources that monitor metals or metal compounds; nevertheless, the next group of sources to have residual risk standards promulgated includes primary aluminum smelters and refineries that regulate metals (National Lime Association v US EPA 2000).

4.6 Long-Range Transboundary Air Pollution (LRTAP)

The issue of air pollution was seen as more of a national issue than a global one. The idea that one country's industrial pollution may contaminate another was controversial. Long-distance air pollution transfer has been identified as a significant element influencing ecosystems and human populations. The research report "Long-Range Transport of Air Pollutants: Measurements and Findings," which the Norwegian Institute for Air Research (NILU) produced for the Organization for Economic Co-operation and Development (OECD) in 1977, was a turning point. This study was critical in determining the extent to which air pollution may spread. The analysis showed that pollution could travel long distances and that national initiatives in a single country can only go so far in reducing acid rain. As proof of the importance of the long-distance transboundary air pollution movement grew, the affected states joined together to create international legislative procedures to lower emissions of the most dangerous pollutants. This led to the 1979 signing of the Convention on Long-Range Transboundary Air Pollution with the intended goal of limiting acid rain's impacts through sulfur and nitrogen emission management. The Convention's scope was later expanded to include ground-level ozone formation (Protocol to Abate Acidification, Eutrophication, and Ground-level Ozone, 1999), as well as persistent organic pollutants (Protocol on Persistent Organic Pollutants (POPs), 2001) and HMs (Protocol on Heavy Metals, 1998).

Long-range transboundary air pollution includes, but is not limited to, acidifying gases like sulfur oxides (SO_x) and nitrogen oxides (NO_x), ground-level ozone, particulate matter (dust), and environmental pollutants such as HMs and persistent organic pollutants (POPs). The influence of long-distance air pollution transmission from far-off sources on global air quality is enormous. Changes in the meteorological conditions during long-distance travel allow for chemical transformations and the formation of secondary pollutants such as ozone, as well as the removal of pollutants by dry or wet processes. For instance, a study was conducted in the southernmost region of Norway to assess the deposition of the most common air pollutants in natural surface soils. These areas had less than a minimum contribution to air pollution; however, it was observed that the pollution levels concurred with the maximum precipitation zones. This might be due to orographic effects (Steinnes et al. 1987).

Based on new scientific data and revised estimates of emissions, air levels, deposition, and environmental destiny, the preliminary assessment of HM health concerns done by LRTAP in 2002 was revised. Data on the danger of these compounds, the propensity for some metals to travel great distances after being discharged into the environment, their persistence and accumulation in different environmental compartments, human environmental exposure pathways, and the results of research on the detrimental effects on human health have been summarized in several reports released by international organizations, like the World Health Organization (WHO) and the International Agency for Research on Cancer (IARC), or governmental organizations, like the Centers for Disease Control and Prevention (CDC) in the United States. Anthropogenic emissions generally outnumber natural

emissions, and despite the present trend toward lower natural emissions, releases into the environment continue to cause modest increases in soil contamination across many regions of the world due to metal tenacity.

4.7 Fate and Behavior of HMs in the Environment

The environment is dynamic. The atmosphere, watershed, land, and living creatures are all impacted by physical changes or incidents that take place on Earth, whether they are natural or manmade. For instance, industrial sectors have been releasing a variety of pollutants, including HMs, into the air, watershed, and land. Multiple environmental compartments will experience infiltration, circulation, and finally agglomeration of contaminants (air, water, soil, and biota). These are referred to as contaminant pathways. They are also depicted as interconnected divisions of the atmosphere, hydrosphere, and lithosphere (Walker et al. 2006). In a short time, the HMs have significantly polluted and accumulated, as well as dispersed and transmitted across the compartments. Investigating their transportation, as well as their destinations and behaviors in the air, water, soil, and biota, is crucial (Pachana et al. 2010).

The localization of a large amount of HM causes an increase in its toxicity. The main channels for chemicals to enter and diffuse into the environment are air and water. The dispersion of lead off the coast of England revealed that it was produced on land, transported by air, and ingested by water and biota. These sources included industries, hazardous waste disposal sites, lead-suspended air conditions, and more (Cheevaporn 2004). Chemical pollution pathways include not only air and water but also soil and biota. Organisms harboring potential carcinogens can compartmentalize them into persistent deposits to stop them from interfering with cytoplasmic metabolic processes (Briffa et al. 2020) but remain persistent leading to bioaccumulation and biomagnification. Due to their nonbiodegradable and persistent nature, HMs cannot be broken down and exist in the sediments and soils for prolonged periods until transferred to some other compartments (Briffa et al. 2020). Transport can take place both within and between compartments. HMs are dispersed after infiltrating the environment and may be converted into different compounds. Photodegradation (e.g., UV), chemical degradation (e.g., hydrolysis), and biodegradation are examples of transformation processes in the environment (e.g., bacterial decomposition). Biotransformation is the process of HMs being converted within organisms (Boonsaner 2006).

As HMs enter compartments, their fates and behaviors have changed and moved between settings (Fig. 4.2). Based on their physicochemical features, the majority of dissolved HMs conveyed by natural water systems are quickly adsorbed by particulate matter (Forstner and Wittmann 1983). HMs can adhere to particulate matter or bond with organic groups to form organometallic complexes, resulting in lipophilic molecules and ions. As a result, they can be found in animals, plants, and sediments. Their destinies and behaviors are governed by sinks and remobilization processes, serving as entering compartments, as claimed by Forstner and Wittmann (1983) and

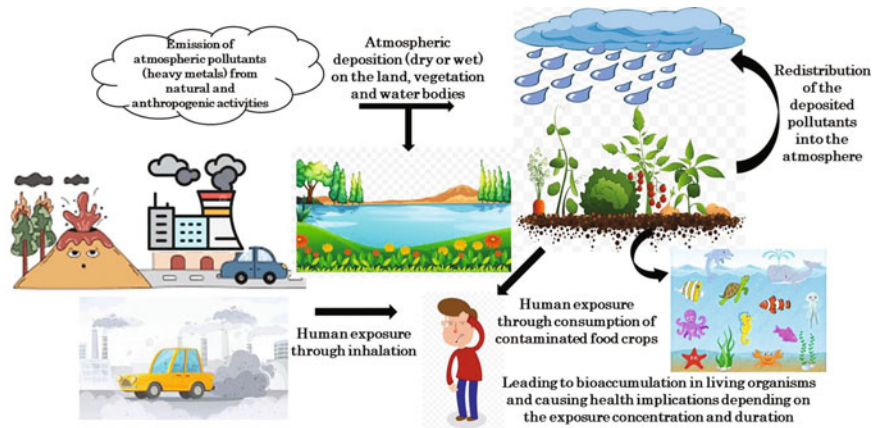


Fig. 4.2 Graphical illustration of the fate of atmospheric heavy metals

Cheevaporn (2004). Sink processes include adsorption and co-precipitation, precipitation, and absorption into biological activity, while remobilization mechanisms include increased salt concentration, redox condition, pH lowering, increased usage of organic complexing agents, and biochemical processes.

4.7.1 Sink Processes

4.7.1.1 Adsorption and Co-precipitation

HMs (Me^+) react in the form of positive ions. The sorptive properties of negatively charged ions, such as carboxyl and phenolic OH^- groups in organic materials, ferrous hydroxide (FeOH^-) and Mn hydroxide (MnOH^-) fractions in hydrous Fe and Mn oxides, silicon hydroxides (SiOH^-), and aluminum hydroxide (AlOH^-) groups in clay minerals, are what cause their adsorption. The preferential adsorption of particular positive charges and the discharge of comparable charges associated with other species are made possible by the selective technique of balancing negative charges (Forstner and Wittmann 1983; Pachana et al. 2010).

Hydrous aluminum, iron, and Mn typically function as significant HM sinks in water systems, particularly the redox-sensitive Fe and Mn hydroxides and oxides under oxidative conditions. Such hydroxides and oxides, which both represent the Fe^{3+} ion and include ferric oxides (Fe_2O_3^-) and ferric hydroxide ($\text{Fe}(\text{OH})_3$), efficiently bind or co-precipitate cations and anions. Additionally, hydrous Fe/Mn oxides could be a significant cause of dissolved metals since sorbed HMs are quickly mobilized in reducing conditions in natural waters (Pachana et al. 2010).

4.7.1.2 Precipitation

The equilibrium constant of solubility product (K_{sp}), which is used to describe a concentrated solution within which a dynamic equilibrium develops among a solid

and its aqueous ions, is different for every metal (Purdue University 2008). When a chemical's solubility product is exceeded, the compound will precipitate until the product of the ionic levels surpasses the K_{sp} value. Precipitation will happen if the solubility product exceeds its K_{sp} value, which is determined by multiplying the results of the ion products (Ratchamongkol Technology University 2008). Precipitation will happen over the saturated solubility if the combined result of the ion products exceeds the K_{sp} value.

4.7.1.3 Integration of Biological Activity

Metals are nonbiodegradable, suggesting their inability to be broken down into less hazardous parts. Organisms detoxify by encapsulating active metal ions in proteins, such as metallothionein (which binds covalently to sulfur), or depositing them in insoluble form in intracellular granules for long-term storage or expulsion in the stool (Pachana et al. 2010).

4.7.2 Remobilization Processes

4.7.2.1 Increased Salt Concentrations

Due to increased salt content competing with HMs, desorption of HMs from solid materials occurs. Cations of alkali earth or alkali metals interact with immobilized metallic ions on solid materials or sediments before being released into the water. These adsorbed metals would be remobilized by desorption or dissolution, according to Forstner and Wittmann (1983).

4.7.2.2 Decrease in pH

The decline in pH causes an increase in solubility. Hydronium ions (H^+) are generated which interact with metallic ions to cause adsorption with sorptive particles, thus releasing metal ions (Pachana et al. 2010).

4.7.2.3 Redox Conditions

Eutrophication causes oxygen depletion in the aquatic systems; however, oxygen is an essential component for biodegradation by organic substances. As a result, the sediment serves as a sink for oxygen, which is supplied through the sediment surfaces at a rate controlled by the following factors: a biological oxygen demand resulting from respiration and metabolic activities in the sediment; a chemical oxygen demand resulting from inorganic elements, such as Fe^{2+} released to the sediment in the reduced state from decomposing biological matter accumulation; and diffusion, which helps control transportation (Pachana et al. 2010).

The oxidizing environment would typically have an Eh value, usually greater than 600 mv (Fitzpatrick et al. 2008). The Eh value drops dramatically in a decreasing environment at a sediment height of about 20 cm. At the same time, between 15 and 10 cm depth, there is a significant prevalence of iron and Mn in the soils (Forstner and Wittmann 1983). HMs are easily remobilized in this environment through the aqueous compartment.

4.7.2.4 Biochemical Process

Microbial processes facilitate the remobilization of HMs adsorbed onto particulate organic matters or sediments. Biodegradation, i.e., the destruction of organic matter into molecular weight components, is an example of a biochemical remobilization process (Pachana et al. 2010).

4.8 Conclusion

HM pollution of the environmental compartments is undoubtedly the most notable effect of our society's advancement. A chemical's hazard is determined by its toxicity, bioaccumulative potential, and persistence in the environment. HMs are deemed detrimental because of these three components: persistence, toxicity, and bioaccumulation. Soils contaminated by atmospheric HMs contain these contaminants on the surface layers of soil for long periods. It is critical to analyze and monitor the quantities of potentially harmful HMs and metalloids in various environmental segments as well as in the resident biota. Because of their high densities, the fates and behaviors would indicate which places should be examined. A rigorous environmental chemistry and ecotoxicology analysis of harmful HMs and metalloids shows that actions should be taken to limit the impact of these elements on human health and the environment and aid in determining the risk of exposure to vulnerable organisms. In terms of particulate matter and HMs, the implementation of Euro standards for automobile emissions and adequate management of industrial emissions will make Indian ambient air clean.

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