



A Comprehensive Evaluation of Heavy Metal Contamination in Foodstuff and Associated Human Health Risk: A Global Perspective

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Abstract

Heavy metal contamination has an adverse effect on the aquatic, terrestrial, and atmospheric environment. These may be natural or anthropogenic in origin and not easily degradable. Anthropogenic activities have unwantedly transferred these heavy metals in our food chain and food web. Directly or indirectly these heavy metals have entered in our food through irrigation by wastewater effluent released by industries; scarcity of available freshwater for irrigation, usage of fertilizers and insecticide, and other anthropogenic activities have caused acute and chronic diseases. The dose–response relationship suggests that the heavy metals have a narrow level of lethal concentrations which pose a threat to the target population. Anthropogenic sources of heavy metals generally dominate natural sources, and foreseeing the synergy of this with the degrading environmental conditions, the health of people is a matter of concern. When these heavy metals get accumulated in the human food, it results in abnormalities affecting human survival and mortality. Recent data suggest that the human body gets affected by heavy metal contamination at lower levels than previously anticipated and evidenced. Agrochemicals are resistant and adaptive in nature, and with the increasing dose and newly synthesized compounds to protect crops, undesired side effects and the costs of food production are on a hike. Practices like street food vending and addition of preservatives in packed food increase the chances of heavy metal contamination in food materials. A comprehensive evaluation of the food chain right from the primary producers to consumer level is necessary to ensure food security and quality.

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2.1 Introduction

The heavy metal pollution is one of the world's top environment-related problem, and has risen due with the increasing industrialization and urbanization. It has become one of a very serious threats due to its deleterious effects on human being and environment (Yang and Sun 2009). With increased economic growth globally in recent years, production and uses of heavy metal has accelerated many folds, leading to pollution of the environment (Raju et al. 2013; Zojaji et al. 2014). Heavy metals have a higher density, atomic weights, or atomic numbers. Due to its adverse effects exposure of heavy metals are always considered as a potential risk to human beings and the environment. Toxic metals such as cadmium, mercury, lead, and arsenic are the main causes of human health problems. Contamination of heavy metals can't be physically identified or distinguished because of its colourless, odourless nature and easily get absorbed. When environmental conditions changes or exceed the tolerance of the environment, heavy metals get converted in to ionic forms, which are active and bioavailable which may act as chemical time bombs and casues serious threat to the ecological system (Wood 1974). Exposure of even lower concentrations of some of these elements are very toxic to the human body and can cause acute or chronic diseases. In the past, only a few cases were reported about soil contamination by some of the specific heavy metals, but in the recent years, presence of various heavy metals have been reported in the each component of the ecosphere (Zhou 1995). Heavy metals may get released in the atmosphere through gases, dust, smoke from various industries, energy production, metallurgy, transportation, and constructional materials. Only mercury in the atmosphere is present in the form of aerosols and gets deposited in the soil by precipitation and natural sedimentation. Heterogeneous contamination of various heavy metals can intensify the lethal contamination concentration. Pollution by heavy metals in the environment has become a significant ecological concern because it takes a longer time period for degradation and has a longer biological half-life (Abii and Okorie 2011). Anthropogenic source of heavy metals includes various activities like pesticide and fertilizer application in the crop field, untreated effluent discharge from industrial activities, mining activities, and sewage irrigation etc. (Zhang et al. 2011). A report from Central Sweden by Lin (1998) stated that environmental pollution by lead is mainly due to urban industries. The lead contamination can spread or get transported by water and winds from the waste heap/dumps to another surrounding area. Lead contamination of ground water also occurs through percolation/leaching of industrial waste.

Another potential source of heavy metal pollution in the agricultural land is wastewater irrigation from sewage and industrial effluents. Due to lack of fresh water resouces, domestic wastewater or industrial effluents are used for irrigation

in urban and peri-urban agricultural practice (Singh et al. 2010). In India, approximately 73,000 ha of agricultural land is irrigated with wastewater (Kaur et al. 2014). Wastewater irrigation when continuously practised may lead to accumulation of toxicants (including heavy metals) in the soil as well as in vegetable crops (Marshall et al. 2007). Contamination of heavy metals in vegetables generally arises from irrigation of polluted water. However, contamination may also occur due to use of chemical fertilizers and pesticides, during the process of harvesting, transportation of vegetables, and the storage. The pollution of the environment is due to human activities owing to the discharge of heavy metals from tanning industries, lubricants used for maintenance of machinery, etc. Contamination of heavy metals in food via consumption can become a risk to human health. According to a report by WHO and FAO (2007), higher concentrations of heavy metals in India were found in milk and drinking water and have exceeded the safe limit. In peri-urban areas, heavy metal contamination occurs mainly through dust and aerosols laden with metals which enter into the soil, and also gets deposited or absorbed by the leaves of the vegetables and plants (Abii 2012; Kachenko and Singh 2006). Vegetable crops grown in surrounding areas of industrial locations have been reported to possess high elevated concentration of heavy metals (Singh and Kumar 2006). The heavy metals get accumulated in the aquatic ecosystem as well which further get transferred in the fishes and other aquatic organisms. When the contaminated water is used for irrigation, the soil gets contaminated and from the soil heavy metals get absorbed by the roots of the plants or crops and get accumulated in different parts of the plants. Through the plants, these toxic metals finally enter into the food chain. The heavy metals contaminated fruits and vegetables when consumed through ingestion, causes various types of diseases and abnormalities in human beings depending upon the degree of contamination. Some of the heavy metals are essential in lower concentration to support vital functions but may inhibit enzymatic activities and pose toxic effects on higher concentrations (Koropatnick and Leibbrandt 1995). In past few decades, human health issues are of major concern with reference to the intake of common food stuffs including fruits and vegetables contaminated with heavy metals (Milacic and Kralj 2003).

Based on the toxicity, some of the heavy metals such as arsenic, lead, mercury, and cadmium ranked first, second, third, and fourth in the list, respectively. Arsenic, lead, and mercury are ranked as the top three most hazardous substances in the priority list of the Agency for Toxic Substances and Disease Registry (ATSDR). Fig. 2.1 presents a schematic representation of sources of heavy metal contamination in the environment.

Cadmium, lead, arsenic, and mercury pose serious health risk when consumed through contaminated food. Cadmium and lead have significant health hazard since these elements are easily accessible to the food chain. Children are more vulnerable when exposed to these elements because they get easily accumulated in tissues and causes retardation in children and adverse effect on the kidneys, cardiovascular system and auditory system (Rahimi 2013).

This chapter provides a detailed overview of heavy metal contamination in foodstuff and associated human health risk. Contamination of foodstuff by heavy metal has

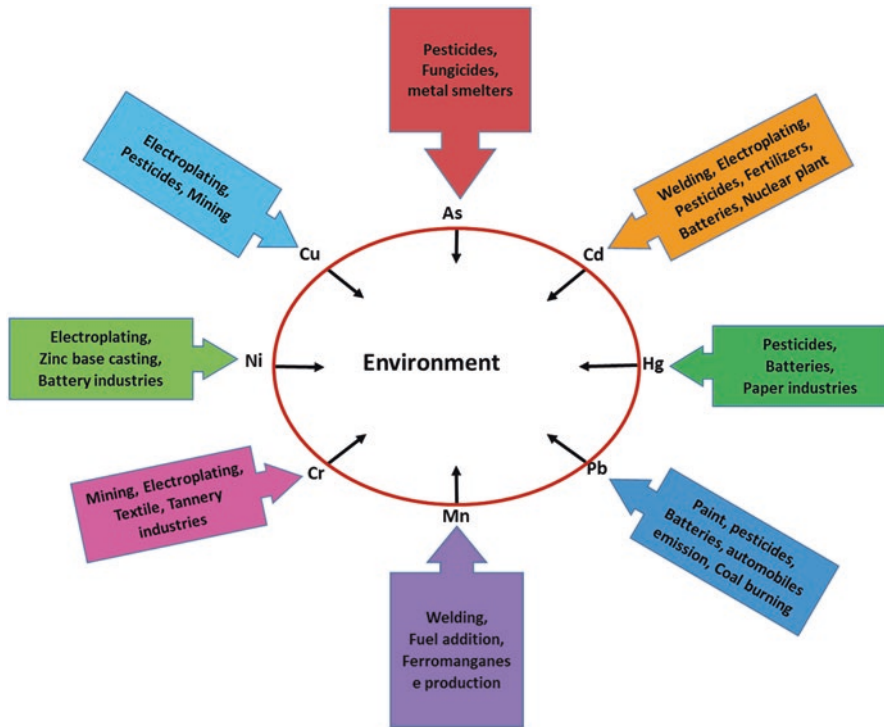


Fig. 2.1 Sources of heavy metals in the environment. (Modified from Paul 2017)

become a global problem. Appropriate prevention measures need to be seriously implemented to avoid metal contamination in food. People consume food on the basis of their social and financial capabilities. The situation in developing countries are more vulnerable, as low-income individuals are unable to afford the good quality food and the right amount of nutrition. The national and international regulatory bodies should attempt to reduce the urban pollution load to reduce contamination in fruits, vegetables, and cereals. The contamination of following heavy metals are most common in foodstuff.

2.1.1 Lead

Lead is a naturally occurring element and is the most commonly used element after iron. No significant biological function of lead in a human being is known. Exposure of lead can be from the air, water, dust, food, and consumer products (Lead poisoning and health 2016). Exposure of high concentration of lead can be poisonous and can affect the health of all ages of peoples. Lead can more severely affect vulnerable population especially infants, young children, pregnant women, etc. Lead contamination in food stuffs is mainly caused by the application of chemical fertilizers and

pesticides or through contamination of soil by sewage and industrial effluents. Once in the food chain, lead can easily accumulated in the human body, which may result in acute poisoning (Tajkarimi et al. 2008). The three main body systems, i.e. nervous system, hematopoietic system, and renal system, are highly sensitive to this metal (Naseri et al. 2015; Zahir et al. 2005). Lead can affect many organs and functional systems of the body; further high exposure can be carcinogenic, damages the brain, and causes miscarriage in pregnant women. Regulatory limits of lead in air and water as per EPA are 0.15 micrograms per cubic metre (for air) and 15 ppb in drinking water.

2.1.2 Cadmium

Cadmium makes up to 0.1 ppm of the earth's crust (Wedepohl 1995). It is a toxic heavy metal present naturally in the environment. Primarily cadmium contaminant occurs from mining, smelting, and refining sulphidic ores of zinc as well as from dust generated by recycling iron and steel scrap (Ayres et al. 2003). Phosphate fertilizers contain varying amounts of cadmium up to 300 mg/kg, and therefore, application of high amount of chemical fertilizers in agricultural soils results Cd contamination in agricultural lands (Grant and Sheppard 2008; Jiao et al. 2004). The high level of cadmium contamination generally occurs in the industrial areas. A significant exposure of cadmium to human beings is also occur by cigarette smoking. Resident residing near hazardous waste dump sites or industries which emit Cd into the ambient air has a potential chance of exposure through respiration of such contaminated air. The Cadmium contamination into the groundwater, soil, and crops which has resulted in adverse health effects such as hypertension, mutagenesis, carcinogenesis, and kidney lesions (Binns et al. 2003). The main culprit of Itai-itai disease is cadmium exposure which is characterized by severe pain in spine and joints. The cadmium poisoning can affect calcium metabolism and results brittle bone and kidney failure (Abbasi 2015). Cadmium poisoning in mass level was first reported in Japan which was occurred due to consumption of contaminated rice grown in river water contaminated by cadmium due to release of mining spealage. The concentration of cadmium should be under 5 ng/m³ in the atmosphere, 2 mg/kg in the soil, 1 µg/L in freshwater, and 50 ng/L in seawater (Rieuwerts 2015).

2.1.3 Chromium

Chromium is a toxic heavy metal that occurs in the environment in oxidation states. Chromium(III) in traces, is an essential nutrient for human biological process. Both chromium(III) and chromium(VI) are stable elements, while chromium(VI) a very toxic form and also carcinogenic i.e. cancer-causing for human beings (Thompson et al. 2012; Costa and Klein 2006) and teratogenic i.e. malformations in a foetus (Xia et al. 2016). The release of chromium is mainly occurs through industries.

such as from tanning, mining, electroplating, and textile industries (Ajmal et al. 1996; Moncur et al. 2005). Coal and oil combustion also leads to release of Cr in the environment (ATSDR 2000). The exposure of chromium to human may be through oral, dermal, and/or through inhalation. The oral intake of these heavy metals is also occurs from contaminated wells (EPA 1998). Exposure of chromium may cause several types of diseases i.e. mouth ulcer, indigestion, acute tubular necrosis, vomiting, abdominal pain, kidney failure, and even death (Beaumont et al. 2008). The maximum concentration level of chromium in water supply should be 0.05gm/L according to Indian standards (Benazir et al. 2010).

2.1.4 Arsenic

Arsenic is a naturally occurring element and is present in water air and soil. Arsenic pollution and toxicity are one of a major global problem. Contamination of arsenic is occur by natural geological sources which results in groundwater contamination. Arsenic contamination also occur due to human activity like mining and industrial processes. It is present in both forms, i.e. organic and inorganic. The major use of As is in the alloys of lead, i.e. car batteries and ammunition. Arsenic is also widely used as a wood preservative. Leaching of As into the groundwater can be through rocks, soil, and pesticides. Volcanic eruptions and mining activities can also lead to the release of As in the environment. Groundwater contamination of As is a global problem. A higher level of As is usually found in the aquifers and less in surface water. Dietary intake of even a very small amount (less than 5 mg) could result in vomiting and diarrhoea (Kingston et al. 1993). Lethal dose of As ranges from 100 to 500 mg which results acute poisoning (Schoolmeester and White 1980). The permissible limit of As in drinking water is 0.01 mg/L as given by the Bureau of Indian Standards.

2.1.5 Mercury

Mercury is the only metal that is present in a liquid state at standard temperature and pressure and is a poor conductor of heat a fair conductor of electricity compared to other metals (Hammond 2005). It is also known as hydrargyrum (Random House Webster's Unabridged Dictionary 2014), a shiny metallic liquid present in trace amount in igneous and sedimentary rocks. Mercury exposure to human beings occur through ingestion, inhalation, and skin contact. Studies have suggested that mercury vapour inhalation can cause immune system disorders, kidney dysfunction, infertility, adverse effects on the foetus, heart failure, and Alzheimer's disease. Exposure to mercury can cause serious health problems and a threat to the early stage of development in children. Toxic effect of mercury is reported in the nervous, digestive, and immune systems and on the lungs, kidneys, skin, and eyes. People are often exposed to mercury in the form of organic mercury, that is, methylmercury, generally from consumption of fishes and shellfish from mercury contamination in seas and oceans (report by the WHO). Also, mercury exposure via food can be

through the consumption of contaminated rice and other food stuff. Mercury poisoning can cause Minamata disease, which is a neurological syndrome. As per recommendations of EPA and Food and Drug Administration (FDA) mercury concentration should be less than 2 ppb in drinking water, less than 1 ppm in seafood as per guidelines of the Occupational Safety and Health Administration (OSHA). The organic mercury should be 0.1 milligrams of per cubic metre of workplace air, and the exposure should not be more than 0.05 milligrams per cubic metre of metallic mercury vapour for 8-h shifts and 40-h work week (OSHA).

2.2 Source of Heavy Metals

Metallic chemical elements that have higher density and higher atomic weight or mass and are capable of causing an adverse effect on human and environment in low concentrations due to its toxic and poisonous effect are generally termed as heavy metals (Lenntech 2014). These are naturally occurring elements found in the earth and rocks. Due to some of the natural but mainly due to anthropogenic activities, once these metals are released, get concentrated in the plants, animals, and human tissues via inhalation and ingestion and sometimes through misshandling or accidents. Chemical elements such as lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag), chromium (Cr), copper (Cu), iron (Fe), and the platinum (Pt) group are considered as heavy metals.

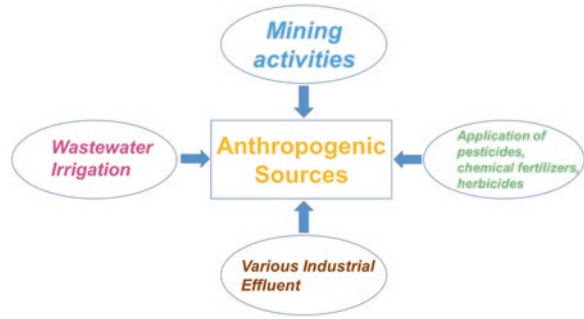
2.2.1 Natural Source of Heavy Metals

Metals have been present in the earth from the beginning of the earth's formation, i.e. billions of years ago (Dalzeil 1999) by the natural process of the biogeochemical cycle. The weathering process of underlying bedrocks is the result of naturally occurring heavy metals in the soil. Mendip region's soil (Great Britain) has been found to be heavily enriched with lead, zinc, and cadmium due to mineralized veins and high concentration of metal deposits in the bedrock (Fuge 1991). Bedrock weathering with slightly elevated heavy metal concentration can result in metal enrichment during soil formation process (Blaser et al. 2000). Both natural and anthropogenic sources are the main causes of increasing heavy metal contamination in the environment. Sources of natural cause can be from windblown soil particles, volcanic eruptions, forest fires, biogenic sources, and sea-salt sprays (Muhammad et al. 2011). Windblown dust naturally emitted is often from the industrial origin (Fig. 2.2).

Fig. 2.2 Natural sources of heavy metals in the environment



Fig. 2.3 Anthropogenic sources of heavy metals into the environment



2.2.2 Anthropogenic Sources

The anthropogenic sources of heavy metal contamination are mining activities; application of pesticides, chemical fertilizers, and herbicides; irrigation of crop fields with contaminated water released by small industries and tanning industries; and use of municipal waste as fertilizers (Alloway and Jackson 1999; Srivastava et al. 2018; Sarkar et al. 2018). Applications of mineral fertilizer that contains trace amount of heavy metals are some of the major sources of heavy metal contamination in the food that we consume (Gray et al. 1999). Other anthropogenic activities are the disposal of waste in farmland (Merian et al. 2004; Srivastava et al. 2015, 2016), traffic emission, use of lead as an antiknock in petrol, cigarette smoking, metallurgy and smelting, aerosol cans, sewage discharge, and building materials (Nriagu 1990; Srivastava et al. 2017) (Fig. 2.3).

2.3 Food Contamination by heavy metals

During the process of food production, packaging, and transport from ‘farm to fork’, there are several possible ways by which the food gets contaminated by various toxicants including heavy metals. Contamination has such potential to migrate into the food and become bioavailable after oral intake. The largest source of food contamination occurs through food contact materials. Plastics, printed papers, and boards are some of the basic food contact materials. These food contact materials are cheaper, durable, and non-porous which makes it primarily the most commercial’s container for storage of food.

As the process of contamination from its primary source was carried in the environment, then contamination level and the concentration of heavy metals transferred into the food chain and food web through different trophic levels. Heavy metals present in the soil, air, and water get accumulated in the plants or animals, and ultimately reaching into the foodstuff. The contamination through human activities, as a result, can affect a large geographical area affecting the environment and human health. The bioaccumulation of heavy metals and their transfer occur from lower

trophic level to the higher trophic level. The concentration is always higher in the higher trophic level.

A study was conducted in Ghana reported that irrigation with water contaminated with Cd and Pb resulted in the accumulation of these heavy metals and showed significant concentration in carrot, cabbage, and lettuce (Odai et al. 2008). The scientists from all over the globe are evaluating the daily intake of such substances from food and their accumulation rate in the human body and are making cautious effort to regulate and control these substances with the help of government and NGOs. Appropriate efforts and strategies are being made to combat and minimize the heavy metals to enter our food chain. Studies have been conducted in indigenous people's traditional diet which has been found to be contaminated by organochloride through marine fish and mammals in their diet especially in New Zealand (Stewart et al. 2011). Certain research has revealed that indigenous communities have elevated heavy metal contamination in the traditional diet (Hoekstra et al. 2005; Johansen et al. 2004; Odland et al. 2003; Van Oostdam et al. 1999, 2003). In the aquatic food chain, heavy metals easily get accumulated in the animals having comparably high lipid contents. An example of an aquatic animal, i.e. eels which are rich in lipid and are at the top of the food chain of New Zealand, were found to have comparably higher accumulation of contaminants (Stewart et al. 2011).

High concentration of heavy metals in the marine animals have drawn the interest in contamination in public food supply, especially in fish (Tariq et al. 1993; Kalay et al. 1999; Rose et al. 1999). Environmental scientists and toxicologists are putting efforts to measure such contamination in our food chain and have estimated the dietary intake and accumulation in our body. There are many regulatory agencies have specific recommendations for the acceptable limits of such contaminants. Heavy metals in food may be found naturally or by environmental contamination or during the process of making the food (Steve Hall 1995; Voegborlo et al. 1999). Aquatic ecosystems near the industries have a significantly greater amount of heavy metals. Even a small concentration of these heavy metals in the ocean has a significant effect on biological productivity. Heavy metal once released in the aquatic ecosystem, it can be distributed and accumulated in the different part of the aquatic biota including flora and fauna. Therefore, most of the species of flora and fauna act as an environmental indicator in the environment and hence monitored for the assessment of environmental risk and pollution load (Jorgenson and Pedersen, 1994; Widianarko et al. 2000). Fish are on the top of the consuming food in the aquatic system (Dallinger et al. 1987). Other than occupational exposure of heavy metals, consumption of fish is the largest source of mercury intake in our diet.

Heavy metals such as methylmercury and mercury have been reported in different aquatic organisms (Pandit et al. 1997). Accumulation of organometallic compounds in superior organisms is due to the high affinity to -SH groups of lipid tissues and proteins in organisms (Pongratz and Heumann 1999). The most common form of mercury found in the environment is methylmercury which is converted from ionic mercury to organomercury and has a potential of causing a hazard (Hintelman et al. 1993; Tripathi et al. 2003). Methylmercury can cause toxicity in the brain, especially in the central nervous system, which may occur at very

low doses i.e. 3.0 µg/kg in humans (WHO 1976). Inorganic arsenic contamination in food has also been a potential hazard to human health because of its carcinogenic effect on human as well as deleterious effects on the urinary bladder, lung, and skin. Studies have revealed that due to anthropogenic activities, higher concentration of arsenic is found in aquatic ecosystems. Therefore, the arsenic exposure to human beings is mainly occur via ingestion of contaminated seafood and drinking water.

2.3.1 Application of Fertilizers and Pesticides in a Crop Field

Due to the rapid increase in the human population, the demand for food in the society has also accelerated, which has increased the demand of application of a huge amount of fertilizers to increase the crop yield. In the same manner, application of insecticide has increased many fold to protect the crops from the pest. Insecticides are not only used in agriculture, but also in the pharmaceuticals and other, industries, and consumer products. Insecticides are claimed to be a major factor behind the increase in the twentieth-century agricultural productivity. Being toxic in nature, most of the insecticides have the potential to significantly alter ecosystems. Most of the pesticides get concentrated in the ecosystem spread along the food chain. A report by Islam et al. (2018) in Bangladesh stated that concentration of Cu, Cr, As, and Cd was higher than the irrigation water quality standard given by FAO. They also identified the problem and concluded that it was due to polluted water and the use of agrochemicals in the agricultural field.

2.3.2 Contamination by Anthropogenic Activities

Heavy metals like arsenic, lead, mercury, and cadmium are toxic and cause neurological problems in developing children (WHO 2017; Tchounwou et al. 2012). Anthropogenic activities like the burning of fossil fuels and mining activities are some of the major of these metals as these metals contaminate the agricultural soil by aerial deposition (Pollution 2007). Subsequently, the plants take up the metals from their root system from the soil resulting in contamination of vegetables and fruits. Urban farming and gardening practices also have contamination in food due to urban pollution.

2.3.3 Food Processing and Packaging

After harvesting, the crops need to be stored appropriately. The food is usually stored in the plastic containers because it is cheap, and easy to handle. But when the food gets in contact with the plastics, some of the chemicals present in the plastics, get leached out and contaminate the food (Radford 2019). Even in the containers madeup of inert materials like ceramic, glass, the chemicals present in these materials can migrate to the food from their inner surface of the containers. Non-inert

materials like adhesives, labels, coating, and inks can also contaminate the food. Canned food is often less nutritious than fresh or frozen food and sometimes get contaminated during storage and transport (Muncke 2016). Sulphites are common preservatives used in various fruits which has adverse effects in the form of palpitations, allergies, headaches, and even cancer in the human beings. Nitrates and nitrites are used as curing agents in meat products. It gets converted into nitrous acid when consumed and is suspected of causing stomach cancer. Benzoates are used in foods as antimicrobial preservatives and have been suspected to cause allergies, asthma, and skin rashes. A serious issue arose when cooking the meat in grills as directly cooking meat and other food products with flames of gas, charcoal, and combusting wood, there are possibilities of getting it contaminated as charcoal and wood emits chemicals during burning known as polycyclic aromatic hydrocarbons (PAHs). PAHs are potential carcinogens and may cause severe damage to the skin, liver, and stomach in the long-term exposure.

2.3.4 Adulteration in Food

Adulteration in food is a common practice by the food producer so that they can increase their profit margin. Some of the common practice in food adulteration is adding water, chalk, urea, caustic soda, and skimmed milk in milk. It is also easy to adulterate oil and fats, which is undetectable. Ghee is often mixed with hydrogenated oils and animal fats. Adulteration in food grain includes the mixing of sand or crushed stone so that the finished food grain product increases the weight. In some vegetables, synthetic colours are used to give it a natural appearance to the consumers. Cheap, synthetic, and chemical colour flavours are used in some food products which are dangerous and may cause allergies to some of the consumers. Such adulteration practices should be strictly monitored and abandoned by the food quality regulatory organizations, and also the people should be made aware as what they are consuming (Radford 2019).

2.3.5 Contamination of Agricultural Soil and Crops by Irrigation of Wastewater

Rapid growth in the human population, industrialization and modern agricultural practices have accelerated the rate of contamination of heavy metals in the environment. Heavy metal contamination in irrigation water and soil from numerous activities such as irrigation of crops from domestic wastewater and industrial effluents are the major concerns. Further, release of untreated effluents in the water bodies, streams, lakes, and the river leading to heavy metal contamination in aquatic bodies and when such water is used for irrigation, agricultural soil and crops get contaminated. Even heavy metals leaching through the contaminated soil and industrial waste can contaminate the groundwater aquifers. Arsenic pollution in groundwater is the major issues in the globe.

The availability of freshwater resources are very scarce which is getting reduced every year and many part of the world are facing water crisis even for the drinking purposes and some of the counties would soon face water scarcity in the near future. Throughout the world, farming depends on river water, lakes, and streams for irrigation. Groundwater is also an alternative water resource, but due to rapid uses, the water table is declining and would be deficient even for drinking purposes. With the increasing use of mineral fertilizers for high production of crops for maintaining the demand of food, unintentionally the groundwater aquifers are getting polluted especially for the nitrate contamination is increasing in drinking water (Schroder et al. 2004; Camargo and Alonso 2006). This is same in the case of almost all the developed and developing countries. In the past, soil contamination was not considered as an environmental problem compared to the air and water pollution. But in recent times, the soil contamination has become a major environmental problem.

The major problem with soil contamination is that, it takes a longer time to remediate (Wood 1974) and is difficult to reverse the effect of numerous types of contaminants through dilution or by self-purification and other techniques. whereas it is comparably easy to manage the water pollution by managing the point sources of pollution. Plants grown in contaminated soil can accumulate heavy metals in their tissues and act as bio-sinks for these heavy metals (Bhatia et al. 2001). Heavy metal contamination in water due to natural weathering of rocks is unpreventable however, contamination due to human activities can be managed up to some extent.

Wastewater use in irrigation is increase many folds in past few decades due to unavailability or shrinking of freshwater resources. The use of wastewater can conserve freshwater, reduce pollution in available water resource, and also provide micronutrients, organic matter, nitrogen, phosphorus, etc. (FAO, 1992; Murtaza et al. 2010; Hanjra et al. 2012). However, heavy metals and some of the organic contaminant not get removed during the conventional wastewater treatment, which subsequently ends up in the agricultural soil through irrigation water and ultimately to the human food chain (Fytianos, 2001). According to a study, consumption of heavy metals via food, milk, and drinking water in India was higher than that of the limits set by the WHO and FAO (2007). Heavy metal contamination in human food chain is shown in the Fig. 2.4.

2.4 Accumulation and Toxicity of Heavy Metals

The heavy metals has been proven to cause health-related issues and a major threat to the exposed population. Due to its ubiquitous nature and tendency to remain in the environment for a long time, thus get accumulated in different component of the environment and poses toxic effects (Gilbert and Weiss, 2006). Heavy metal exposure and toxicity can be divided into chronic and acute toxicity. Once metal contamination occurs in the biological system, certain metals can combine with the sulfhydryl group, inhibiting various enzymes and processes in the biological process, due to its high-affinity properties (Jan et al. 2015). Chronic exposure of heavy metals can induce neurotoxicity and hepatonephrotoxicity (Caito and Aschner 2014).

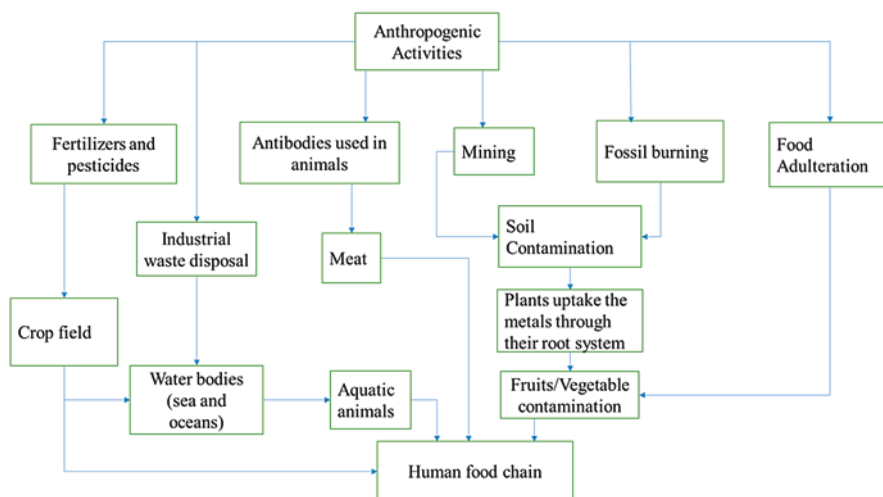


Fig. 2.4 Flow chart of heavy metal contamination in human food chain

2.4.1 In Agricultural Crops and Plants

The pathway by which the heavy metal ions enter through the food crops is from the root system of the crops, i.e. apoplast and symplast movements. These two movements are two different pathways by which water and metal ions pass through the root hair via the root cortex to the xylem. In the apoplast movement, more ion and water are transported through the apoplastic pathway (inner cellular space) in the cortex, whereas in symplast movement, water and ion are mainly delivered through the symplastic pathway beyond the cortex. Heavy metal movement occurs generally in the symplastic pathway, i.e. through crossing the plasma membrane (Peer et al. 2006). Further, the metal ions are facilitated inwards by the electrochemical gradient (Raskin et al. 1994). When the metals reach the xylem, the metal transport is mediated by the membrane transport protein (Thakur et al. 2016). Arid and semi-arid regions with short wet seasons and long dry seasons, rely on unconventional water resource and are being used to fulfil the increasing demand for food for the society. Vegetables/crops grown in wastewater irrigation-contaminated soil accumulate a significant level of heavy metal concentration than that grown in soils irrigated with freshwater (Balkhair and Ashraf 2016). A study by Khan et al. (2008) concluded that irrigation with untreated irrigation water increases Pb, Ni, and Cd concentration in the crops and poses an adverse effect on the health of humans. Leafy vegetables can accumulate comparably a higher concentration of heavy metals when grown in a site contaminated by heavy metals that are absorbed mostly in the leaves of the vegetable (Jassir et al. 2005). Vegetables like cauliflower, spinach, and cabbage can even grow well in a high level of heavy metal-contaminated soils and wastewater irrigation (Cobb et al. 2000), whereas some of the vegetable like radish is more sensitive to sewage water (Kapourchal et al. 2009).

Heavy metal uptake by food crops depends upon soil physicochemical characteristics and plant species (Zhuang et al. 2009). Bai et al. (2010) reported that cultivation history is an important factor related to the accumulation of heavy metals, particularly of Cu, Pb, and Zn. Heavy metal uptake in crops majorly depends on the temperature, moisture, pH, organic matter, nutrient availability, plant species and their uptake potential, or soil-to-plant transfer factors (Tangahu et al. 2011; Khan et al. 2008).

Elevated heavy metals in soil can result in a decline in soil productivity; lower the development process which are vital for plant growth like photosynthesis, mitosis, and water absorption; and lead to stunted growth of plants/crops (Bhattacharyya et al. 2008). Use of municipal waste, sewage sludge in the agricultural field is a general practice in developing nation worldwide to lower the cost of fertilizers. However, applications of waste and sludge may contaminate the soil and groundwater quality and may increase poisoning in the food chain.

2.4.2 In Aquatic Animals

Burning of coal, smelting, and industrial waste disposal into the seas and oceans are the main causes of pollution in ocean water (Global Mercury Assessment 2013). Due to this, the aquatic life in the seas and oceans are severely getting affected. Mercury has been the main contaminant in fish, inorganic and organic mercury disposed into lakes and rivers may be transformed into methylmercury, and the mercury levels found in fish, even from 'non-contaminated' areas, are higher than in most other foods. These get absorbed in algae and get biomagnified by the large fish and ultimately get into the human food (Mercury Levels in Commercial Fish and Shellfish 1990–2012).

A report from Guallar et al. 2002 [85] stated that high contamination of metals in fish have an adverse effect on many vital organs of human beings. As per a report from Lake Ontario, decline in woman fertility was observed due to the consumption of contaminated fish (Buck et al. 2000). Similarly, persistent organic compound is found in the aquatic environment, get accumulated in the fatty tissues of fish and passes through the food chain to higher trophic level (Håstein et al. 2006). Due to consumption of fish contaminated with the organochlorine compounds presence of such compounds has been reported in the human lipids and tissues and even in breast milk in women in the countries like India, Japan, and Argentina (Muñoz de Toro et al. 2006; Tsukino et al. 2006; Someya et al. 2010). Organic mercury has higher toxicity than inorganic mercury because of its high solubility in lipids and low rate of elimination which causes bioaccumulation in the organisms (Díez 2009). In the aquatic system, heavy metals exposure to the organisms occurs through their food along with water (Phillips 1995). It was observed that fish accumulate comparably higher concentration of metals when the number of phytoplanktons are high in the region than the areas where the density of planktons are low. Heavy metal accumulation in the flora and fauna increases over the time. Summary of the concentration of heavy metals in agricultural soil irrigated by wastewater is presented in the Tables 2.1 and 2.2 provide a summary of heavy metals in various types of vegetables.

Table 2.1 Summary of the concentration of heavy metals in agricultural soil irrigated by wastewater

Type of water	The concentration of metals (mg/Kg) in soil irrigated with wastewater										Country	Year	
	Cd	Cr	Cu	Pb	Ni	Fe	Mn	Zn	As	Hg			
<i>Domestic wastewater</i>													
Urban wastewater		118.90	39.44		39.75			50.07				Spain	Martinez-Cortijo and Ruiz-Canales (2018)
Wastewater	1.76	42.19	32.68	12.04			277.62	68.75				Iran	Cheshmazar et al. (2018)
Leather industry	0.45	976		50.32					1.94			Bangladesh	Mottalib et al. (2016)
Gold mining	2.867		106.10	723.50				452.90	15.81	12.195		China	Xiao et al. (2017)
Peri-urban industrial	0.605	57.65	5.405	37.6	88.90		359.55	151.3				India	Chabukdhara et al. (2016)
Smelting	7.52		128.7	1090.0				820.0	903.5			China	Zhou et al. (2016)
<i>Domestic as well as industrial wastewater</i>													
	1.42	63.48	107.65	213.93	34.75			427.80				Spain	Zimakowska- Gnoinska et al. (2000)
	0.78		95.00	23.00	57.00							America	Han et al. (2002)
			65.00	139.00	29.00			140.00				Slovakia	Wilcke (2005)
	13.5	48.5	48	55	29			88.5				USA	Jean-Philippe et al. (2012)
	0.82	2.19	1.20	0.95	4.34			28.24				India	Raju et al. (2013)
	0.34	10.36	9.62	5.17	11.28			11.56				Iran	Sayyed and Sayadi (2011)

Table 2.2 Summary of heavy metals in various types of vegetables

Type of vegetable	Concentration of metal (mg/kg)										Country	Author and year of publication
	Cd	Cr	Cu	Pb	Ni	Fe	Mn	Zn	As	Hg		
<i>Leafy green</i>												
Lettuce	<0.005	0.23	0.505	0.016				0.345	0.005	<0.008	China, Spain	Khan et al. (2008) and Ercilla-Montserrat et al. (2018)
Spinach		2.9	0.09	3.1	3.2		10				India	Chary et al. (2008)
Red amaranth	<0.1	<0.1		1.036	0.840	136.3	5.720	11.305	<0.1	<0.03	Bangladesh	Tasrina et al. (2015)
Beetroot	0.09	0.21		0.58	0.26						São Paulo, Brazil	Guerra et al. (2012)
<i>Cruciferous</i>												
Cabbage		0.23	0.505	0.016				0.345			China	Khan et al. (2008)
Cauliflower	0.014	0.02	0.6	0.03	0.68			5.45			China	Song et al. (2009)
Brussels sprouts												
Broccoli	0.08	0.48		0.93	0.26						São Paulo, Brazil	Guerra et al. (2012)
<i>Marrow</i>												
Pumpkin	0.01	1.45		0.25					0.02		Dhaka, Bangladesh	Islam et al. (2014)
Cucumber			0.38	0.031				1.30			China	Xiu-Zhen et al. (2009)
Italian zucchini	0.04	0.08		0.51	0.25						São Paulo, Brazil	Guerra et al. (2012)
Paulista zucchini	0.04	0.15		0.59	0.23						São Paulo, Brazil	Guerra et al. (2012)
<i>Root</i>												
Potato	0.015	0.03	1.03	0.067	0.054			3.77			China	Song et al. (2009)
Sweet potato	0.14	0.04		0.46	0.18						São Paulo, Brazil	Guerra et al. (2012)
Carrot	<0.1	<0.1		0.304	<0.1	8.824	1.257	1.206	<0.1	<0.03	Bangladesh	Tasrina et al. (2015)

Yam	0.06	0.20	0.72	0.20					São Paulo, Brazil	Guerra et al. (2012)
<i>Edible plant stem</i>										
Celery	0.05	0.14	0.47	0.19					São Paulo, Brazil	Guerra et al. (2012)
Asparagus bean	0.013	1.999	0.07		6.682	0.047			South China	Zhou et al. (2016)
Kidney beans	0.010	1.310	0.033		5.669	0.05			South China	Zhou et al. (2016)
<i>Allium</i>										
Onion	0.02	0.07	0.49	0.06					São Paulo, Brazil	Guerra et al. (2012)
Garlic	0.09	0.29	2.50	0.42					São Paulo, Brazil	Guerra et al. (2012)

2.5 Human Health Risk of Heavy Metals

Heavy metal toxicity is generally by cadmium, chromium, lead, mercury, and arsenic, and their exposure is commonly occur mainly through consumption of contaminated foodstuff, and through the contaminated environment. Toxicity of these heavy metals results from sudden, acute, or chronic exposure over a period of time. Symptoms of heavy metals toxicity depend upon metal absorbed, metals involved, and age of the person exposed to these metals. Cadmium particles or fumes can cause acute pulmonary effects and even the death of an individual (Seidal et al. 1993; Barbee and Prince 1999). Kidney damage is generally due to the heavy exposure of cadmium. Several reports have suggested that the kidney damage or bone effect in human can arise even from the exposure of a lower concentration of cadmium. High exposure of cadmium for the longer period can lead to skeletal damage, which was first recorded in Japan in the 1950s and it was named as ita-itai disease. This disease was occurred due to exposure through consumption of cadmium contaminated rice grown on a field irrigated with the contaminated water. The International Agency for Research on Cancer (IARC) has grouped cadmium as a human carcinogen (group I). Cadmium exposure can also cause prostate cancer.

Inorganic mercury acute poisoning can lead to lung damage, while chronic poisoning can cause neurological and psychological disorders, such as restlessness, tremor, changes in personality, anxiety, depression, and sleep disturbance. These symptoms are reversible only when the exposure has stopped, and the same can be observed for metallic mercury which causes kidney damage. Methylmercury poisoning can last from 1 month or longer even after acute poisoning, and it's main symptom is the damage of nervous system. Exposure of a higher dose of methylmercury can cause death of a person. Minamata disease was recorded due to dietary exposure of fish contaminated by methylmercury. The contamination of methylmercury in fish occurred due to the discharge of mercury in the water bodies. In the early 1970s, a similar incidence was occurred in Iran, which caused the death of around 10,000 people due to the consumption of baked bread which was prepared from mercury-contaminated grains.

Lead is also get accumulated in liver and kidney of aquatic animals; consuming this lead-rich diet can cause an unacceptably high level of lead in the human body. Lead contamination in food also occur through food containers like ceramic vessels with lead glaze, storage in lead-soldered cans and leaded crystal glass. Headache, irritation, and abdominal pain are some of the acute symptoms of lead exposure. Sleeplessness and restlessness are some mental disorders which are caused by lead encephalopathy, and children may also suffer from concentration loss, learning difficulties, and behavioural disturbances. Acute confusion, psychosis, and reduced consciousness are observed in adults who may suffer from lead encephalopathy. Lead is classified as a 'possible human carcinogen' by International Agency for Research on Cancer (IARC), in 1987. The upper limit for blood lead for adults is 10 µg/dl (10 µg/100 g) and for children, 5 µg/dl has been set by the Centers for Disease Control and Prevention (USA) (ACCLPP 2012; CFR USA 2005). The evidences from previous studies has revealed that lead poisoned people may suffer

from lung cancer, stomach cancer, and gliomas (Steenland and Boffetta 2000). In the most developed nation, over 540,000 people have died due to the exposure of lead in the year 2016 (Lead poisoning and health 2016).

Acute toxicity of inorganic arsenic intake in large amount can cause gastrointestinal symptoms and disturbances in the cardiovascular system and central nervous systems and may lead to the death of an individual. Arsenic encephalopathy, bone marrow depression, polyneuropathy, haemolysis, hepatomegaly, and melanosis are also observed due to arsenic poisoning. Black foot disease in Taiwan is caused by drinking water contaminated by arsenic which damages the lower limbs resulting in progressive gangrene. A report from WHO on arsenic exposure via drinking water suggests that it may cause cancer in the lungs, kidney, bladder, and skin as well as precancerous lesions in the skin (WHO 2001).

Hence, these heavy metals have the potential to cause disease, cancer, or even death of the person if exposed of heavy metals through diet, inhalation, and/or dermal exposure. The exposure to heavy metals and its toxicity to human beings is one of the major issues for regulatory bodies, organization, and government bodies. The chemical toxic agency should provide ways by which such exposure can be minimized and also provide appropriate tools and techniques to reduce the level of heavy metals in the environment and prevent these metals from reaching it into the human, animals, and the environment in the future.

2.5.1 Carcinogenic Risk Due to Heavy Metals

A recent study that was carried in Palestine by Al-Khatib et al. (2019) predicted that the local residents especially children might have a higher chance of developing cancer due to the presence of Mg, Ba, Fe, Sr, K, Na, and Mn, and their values were greater than the standard limits, i.e. $>10^{-6}$. High level of groundwater contamination near the industrial waste site and municipal solid waste dump site due to poor management was reported in Chandigarh, India (Ravindra and Mor 2019). This study revealed that deeper aquifer was less contaminated than the shallow aquifers. The shallow aquifers are generally used for drinking and irrigation purposes which might directly or indirectly exposed human beings to those of the heavy metals.

2.5.2 Noncarcinogenic Risk of Heavy Metals

A recent study conducted in Iran and revealed that heavy metals like Zn, Fe, Al, Pb, Ni, Cd, Mn, As, and Cr were more accumulated in the medicinal plants than herbal plants and only Hg and Cu were found to be higher in herbal plants and its target hazard quotients (THQ) were less than 1 which is considered to be safe for consumption (Kohzadi et al. 2019). Fluoride contamination in Iranian drinking water was estimated to be low and does not had any carcinogenic risk for both adults and children, but fluoride contamination in food and air was high and had significant effect on human health (Keramati et al. 2019). Heavy metal contamination on

crayfish, meat, fish, and cow skin was estimated in Nigeria, and it was found that the hazard index of raw, smoked, and cooked meat showed the greater noncarcinogenic adverse health effects (Taiwo et al. 2018). A study conducted in India also reported noncarcinogenic risk due to high arsenic contamination in Indian rice (Sharafi et al. 2019).

2.6 Pathway/Exposure of Heavy Metals

Heavy metal exposure to human beings is often from ingestion, dermal exposure, and inhalation (Asaduzzaman et al. 2017; Li et al. 2017). The exposure of heavy metals is usually occurred mainly through the contaminated drinking water and food. Mercury accumulation in human tissues has higher concentration through consumption of aquatic organisms, i.e. seafood, fishes, etc., in the form of methylmercury (Horvat et al. 2003). The main source of mercury intake in diet of the population is from fish as stated by Boudou et al. (2005).

2.6.1 Ingestion

The occurrence and level of contamination, chemical forms, and metal solubility are some of the factors affecting the absorption of trace metals through the gastrointestinal tract. Ingestion is the primary route of heavy metal intake through diet, and it contributes up to 90% of daily dietary intake compared with inhalation and dermal exposure (Loutfy et al. 2006). For example, arsenic exposure is through food and water, and the daily intake ranges from 20 to 300 $\mu\text{g}/\text{day}$ (WHO 2010) depending upon the food type, food processing, and agricultural conditions (IARC 2012). The heavy metals are absorbed and accumulated in leafy vegetables (Arora et al. 2008). Exposure of chromium from food is through meat, molluscs, and crustaceans (U.S. EPA 1998). Kusiak et al. in 1993 have reported that even Cr (III) causes oral toxicity in humans.

2.6.2 Inhalation

Inhalation of heavy metals is considered another pathway of occupational exposure. In the metal plating and some of the other industries, chromium exposure occurs in both forms i.e. Cr(III) and Cr(VI). During inhalation, the Cr(III) gets absorbed in the tissues of the lung due to the reduction of Cr(VI) to Cr(III) (Flaherty, 1996). Chromium is responsible for wheezing, coughing, asthma, and other respiratory diseases (Langard, 1980). The Cr(IV) can even cause cancer in humans even via inhalation route and is classified as carcinogenic material (group 1) by international nodal agencies (IARC, 2012; Waseem and Arshad 2016, 198). Mercury present in the gaseous state, contributes to 80% of the atmospheric mercury (Wang et al. 2004).

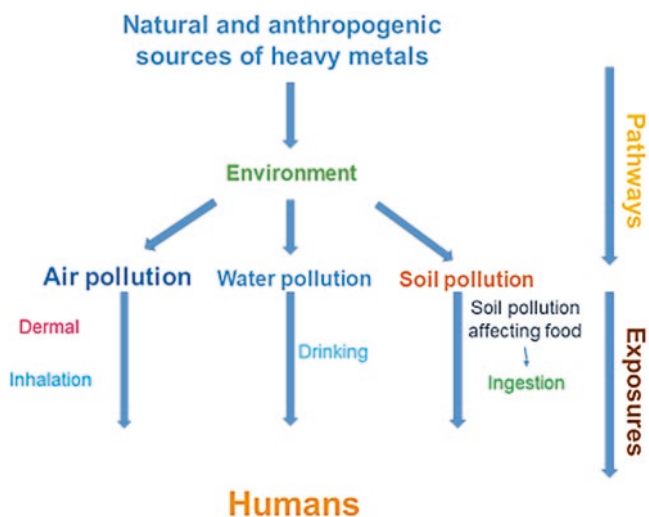


Fig. 2.5 Pathway/exposure of heavy metals in human beings and in the environment. (Modified from Thompson et al. 2012)

2.6.3 Dermal Exposure

The dermal exposure of heavy metals usually occurs when the large surface area of the skin get in to the contact of metal laden dust and fine particles. These small particles sometimes get deposited into the dermal layers of the skin and reached to the circulation system (Li and Zuo et al. 2013, Keshavarzi et al. 2015). The skin is the primary and effective barrier for the absorption of any substance, therefore, only few of the metals that have the ability to penetrate through the dermal layers of the skin, get absorbed. A report by Brandão and Gontijo (2012) stated that nickel metal exposure through the skin has become sensitive to human and is causing allergy in children, especially in developed nations. The exposure pathways of heavy metals is presented in the Fig. 2.5.

2.7 Preventive and Mitigation Measures

Mining, industrial process, and other human activities release several types of chemicals and waste containing heavy metals, in to the environment. Then the metals spread in and around the polluted site polluting the nearby areas. To prevent these heavy metals from polluting the area, the primary release of such type of metals or use of heavy metals in the form of pesticides or fertilizers in the environment should be carefully monitored and regulated. Appropriate waste management system should be adapted in mining areas and industries so that the disposal of such

heavy metal waste can be prevented so that metals are not released into the environment. The major problem also lies in the disposal of untreated wastewater, sewage water, and industrial effluents into the river and water bodies, which further affects the aquatic ecosystem and also contaminating agricultural soil as well as the food crops once used for irrigation. So proper waste treatment plans should be adapted in industries and disposal of untreated effluents must be stopped. A proper waste disposal can prevent the heavy metals released in the environment.

Apart from preventive measures, sites that are already polluted should be reclaimed and should so that further harm to the environment can be prevented. Some are several mitigative measures that can be adapted to reclaim the polluted sites and bring back its original state. Some of them are as follows.

2.7.1 Excavation

It is the easiest, oldest physical remediation method for reclaiming contaminated soil. It is practised all around the world for the management of contaminated soil. The advantage of these methods is that the contaminated soil is completely removed and the contaminated site is rapidly cleaned (Wood 1997). The disadvantage of excavation is that while removing and transferring the soil from one place to another place, it should be monitored or else if the polluted soil spread by any means, it will contaminate another site. Soil with a large area of contamination requires a large area to be excavated. Therefore, this technique is very costly and time-consuming.

2.7.2 Stabilizing Metals in the Soil

Heavy metal-contaminated soil once excavated moves into another site for the stabilization process. This is another way by which their toxic effect can be reduced or their adverse effect can be minimized within a confined area (in situ). This process does not affect the environment or generate toxic waste; instead it lessens the toxic effect of the heavy metals with the help of added chemicals which can detoxify the pollutant. Adding phosphate fertilizer in the polluted soil can neutralize its toxic effect, especially for the sites contaminated with a high concentration of lead. Some other chemicals are also used to bind with the pollutants released form a mineral make a stable compound which is insoluble in water. These methods immobilizes the toxicants to the food chain, and once the metals biologically unavailable, they are harmless to the environment (Lambert et al. 1997).

2.7.3 Use of Plants

Some plants have special ability to reduce the toxic effect in areas and used in situ remediation of contaminated soil, air, and water and is often termed as phytoremediation (EPA 1998). Phytoremediation has certain advantages and is a widely accepted as a low-cost technique for remediation of the degraded, contaminated site (Schnoor 1997). Disadvantages of phytoremediation are that it takes a bit longer time for remediation. Sites that are contaminated can be revegetated with the help of some of the specific plant species, and this process is called phytostabilization. Plants help reduce wind erosion and soil erosion and also help in reducing the materials spreading from one contaminated site to another site. Another way by which plants can be used for cleaning up contamination is phytoextraction. Some plants have the ability to uptake certain heavy metals and concentrate them into their tissues. These plants can further be harvested and disposed of in safe places without harming the environment. Plants like Indian mustards, alfalfa, cabbage, juniper, tall fescue, and poplar trees have potential to accumulate heavy metals and do not possess any harm to the environment and any living organisms. Indian mustards can cure lead contamination in the soil. A rhizofiltration process is another technique used for remediating heavy metals in water bodies in which the roots of the plants directly remove the contamination with the help of some aquatic plant species or hydroponic methods (EPA 2000). Sunflower plants were used to remove radioactive metals in the water lakes of Chernobyl, which is an example of the rhizofiltration technique.

2.8 Conclusion

Food contamination with heavy metals has become a major problem all over the globe and has an adverse effect on human health and the environment. Heavy metals have been on the earth naturally. However, their release in the environment has been accelerated by human activities leading to pollution in the environment. These pollutants are nondegradable and have reached into our food chain and food web, resulting in abnormalities in the metabolism of humans leading to acute and chronic disease or even death. Local people residing nearby areas of pollution site should be made aware of the deleterious effects of the pollutants released and how that can be a threat to their life. The cultivation and production of food crops near area contaminated with a high concentration of heavy metals must be banned. Due to the scarcity of available freshwater, wastewater irrigation is used as an alternative source for irrigation. Unfortunately, continuous use of wastewater is also a prime cause of heavy metal pollution and contamination of food crops. Pollution in water bodies have also become an environmental concerns because water is the only source of survival for living organisms and the survival depend upon water before prehistoric time. In view of this, rainwater harvesting and watershed management must be adapted to harness the freshwater resource which could be utilized for farming.

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