# Chapter 1 Concerns and Threats of Heavy Metals' Contamination on Aquatic Ecosystem



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## 1.1 Heavy Metal Sources

Heavy metals (HMs) gain their entry into the environs by natural plus anthropogenic sources, thereby impairing the soil, water, and air plus their interface considerably if they are present above certain level. Figure 1.1 shows heavy metal sources and their cycling through various components of environmental settings (Brady et al. 1994).

# 1.2 Natural Sources

Most studies have reported various natural sources of HMs. The discharge of HMs by natural sources depends on certain environmental conditions. These sources comprise of emissions from volcanoes, sea salt, natural forest fires, breaking of heavy metal containing rocks, biological sources, and windblown soil particles. Heavy metals are released as hydroxides, oxides, sulfides, sulfates, phosphates, silicates, as well as in the form of organic composites. These toxic HMs enter the water bodies and change the water chemistry, thus affecting the aquatic biota present there. The most common HMs are Pb, Ni, Cr, Cd, As, Hg, Zn, and Cu. Even though

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Fig. 1.1 Sources of heavy metals with their cycling in the environment. (Brady et al. 1994)

they are present in trace quantities, these metals have extreme consequences on all organisms (Herawati et al. 2000).

## **1.3** Anthropogenic Sources

Anthropogenic activities are chiefly behind HM pollution. The main sources are untreated water discharge from industries, agricultural inputs, and domestic effluents; mining and metallurgical processes all add a bulk of HMs into the environment. The introduction of these HMs into an ecosystem due to anthropogenic activities has changed the natural fluxes of these metals. Some significant HM contaminants released from anthropogenic sources which considerably add to the biosphere include lead from vehicular exhaust; arsenic, copper, and zinc from smelting processes; arsenic by insecticides; and nickel, vanadium, mercury, tin, and selenium released from combustion of fossil fuels. To meet the needs of rising human population, humans have significantly contributed to the environmental pollution (He et al. 2005; Bhat et al. 2017)

## **1.4 Pollution by Heavy Metals**

Presently, environmental pollution is among the most paramount existential challenges to mankind. HM presence in the environment at such high concentrations poses a great danger to the environment and may harm environmental components if they are present above certain levels. The combination of population growth and economic development has resulted in amassing of hazardous amount of HMs in the environment. In addition to this, heavy metal mobilization as well as transport in the surroundings has significantly augmented ever since 1940. The HM enters the water bodies via numerous means like effluent/waste discharges, surface runoff, and leachates besides atmospheric depositions through various activities taking place in urban and industrial areas. HMs are often cumulative toxins and strongly affect people when ingested. Accumulated toxic substances tend to increase in concentration and are often present in single tissue (Ansari et al. 2004). The bioaccumulative potential of HMs can result into a wide-ranging concerns fluctuating from molecular alterations to elimination of local fish populations (Massaquoi et al. 2015). Moreover, the existence of deadly concentrations of HMs in bottom-dwelling species has considerably decreased their diversity and affected their development as well as reproductive potential. Sediments cast a noteworthy role in growth, development, and evolution of aquatic beings in addition to acting as a pollutant sink. River hydrodynamics and biogeochemical cycles, besides environmental settings, are among the various processes which govern the dynamics of toxic pollutants in the aquatic ecosystem.

#### 1.5 Heavy Metal Pollution in Aquatic Environs

Heavy metals are among the leading hazards to both terrestrial and marine habitats (Slaveykova and Cheloni 2018). Once they are discharged from natural and anthropogenic sources, HMs contaminate water bodies, underlying sediments, air, and the soil (Singh et al. 2018). HMs gain their entry into the air by volcanic eruptions and from industries. This ultimately reaches to the land, thereby resulting in water and soil pollution. Due to its persistent nature in the environs, HMs either accumulate in biota or are leached into groundwater. Globally heavy metal pollution is becoming a grave subject of alarm as it has protracted motivation due to the rise in the usage and handling of HMs during numerous activities to encounter the requirements of the fast increasing populace. Heavy metal concentration in various environments is ruled by its dose plus the contact period (Khan et al. 2011). Hydrosphere, lithosphere, and biosphere are the chief notable constituents of the environment being affected by heavy metal pollution.

#### **1.6 Effect on Water**

Heavy metals released from different sources contaminate the water bodies. It is an environmental concern that has a negative influence on flora, fauna, and human well-being (Rezania et al. 2016). Even at lower quantities, heavy metals pose extreme danger to aquatic species (Akif et al. 2002). HMs can be a source for chief

histopathological modifications in bodies of aquatic creatures such as fish (Ahmed et al. 2014). Industrialization and urbanization are the two most important sources which have contributed significantly in the heavy metal water contamination. HMs are transported to the water bodies through effluents from industries and sewage inputs besides from agricultural runoff (Afzal et al. 2018), most of which finish up amassing in the soil plus in sediments too (Musilova et al. 2016). The influx of industrial effluents into the aquatic bodies is the principle origin of surface water plus groundwater contamination (Afzal et al. 2018). Effluents from mining operations also result in accumulation of HMs in the aquatic settings (Zhuang et al. 2013). Because of their environmental persistence and bioaccumulation and biomagnification of HMs in food chains, they have become a worldwide problem (Rajaei et al. 2012). Even its presence in smallest amount in aquatic environments can be much toxic to humans as well as other species plus posing serious health challenges. The metal toxicity level depends on various factors like its type, biological functioning, and duration of exposure to the toxic metal. In fact, all aquatic organisms get affected by the contamination of heavy metals. Humans are much susceptible to serious health issues due to the process of biomagnification (Lee et al. 2002) and its presence at upper trophic level. The health impacts of heavy metals are listed in Fig. 1.2.



Fig. 1.2 Heavy metal impacts on human health

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## 1.7 Sediments

Sediment in the aquatic systems is the chief repository and source of HMs. Sediments execute a substantial role in the relocation and in storing of potent toxic heavy metals (Yan et al. 2010; Gao and Chen 2012). It is like a needle pointing to the fact that the water is polluted (Zahra et al. 2014). Sediments are the sink and source of HMs, liberating the HMs into the water column back upon any disturbance (Fernandes and Nayak 2012). The HM buildup in sediments nearby inhabited zones can deliver the confirmation of the human influences on this ecological unit and aids in evaluating the threats linked with the discarding of human waste (Demirak et al. 2006; Balls et al. 1997). Sediments contaminated with HMs are an environmental concern having consequences on aquatic species plus human health. Unending accretion of HMs in sediments may likewise add to the pollution of groundwater (Sanyal et al. 2015). A number of physical and chemical factors regulate the adsorption, desorption, and content of HMs in sediments. These factors include temperature, hydrodynamic settings, redox conditions, number of microbes, salt levels, as well as size of sediment particles (Zhao et al. 2014). In addition to these physical and chemical factors, concentration of HMs in sediments is dependent on chemical composition and concentration of organic matter (Azadi et al. 2018). The bioavailability of metal in sediments has a relationship with the pH also. pH decline impacts binding of metal ions and H<sup>+</sup> in sediments resulting in dissolution of metal complexes, thus liberating free heavy metal ions into the water (Nowrouzi et al. 2014). In riverine sediments, if concentration of heavy metals is high, it may be an ecological risk to benthic organisms (Decena et al. 2018).

#### 1.8 Heavy Metals: Bioavailability and Biological Role

Bioavailability of heavy metals is regulated by physical, chemical, as well as biological factors. The physical factors are temperature, phase association, adsorption, and sequestration. The chemical factors are speciation at thermodynamic equilibrium, complexation kinetics, lipid solubility, and octanol/water partition coefficients (Hamelink et al. 1994). Biological factors like species features, trophic connections, and biochemical/physiological variation are influential (Verkleji 1993). In biological systems, it has been reported that heavy metals impact cellular organelles and other constituents like cellular sheath, mitochondria, lysosomes, endoplasmic reticulum (ER), nucleus, and other metabolism-affecting enzymes and detoxification, besides cellular damage repairing (Wang and Shi 2001). Metal ions also influence cellular constituents like DNA and nuclear proteins, resulting in DNA interference plus conformational adjustments leading to the modification of the cell cycle, mutagenesis, or apoptosis (Chang et al. 1996; Wang and Shi 2001; Beyersmann and Hartwig 2008). The accumulation of lethal substances may result in biomagnification in animals. In aquatic ecosystems, heavy metals of utmost alarm are Cu, Zn, Hg, and Pb as well as Al, Cr, Se, Ag, Ar, and Sb. These heavy metals have magnified the issues associated with the aquatic systems (freshwater, coastal, as well as estuarine ecosystems). These heavy metals when present in a concentration exceeding the threshold are detrimental to organisms although few of them like copper and zinc are vital for metabolism at lesser concentrations.

Few heavy metals don't have any influence on any biological processes of living beings. They remain there in the body in the harmful form and elicit harmful effects, thus affecting their biology. HMs cause biotoxic effects (effect of HMs to the body of living organisms when ingested above recommendation limits) as they interact with the body's natural biochemistry in the normal metabolic processes. Most HMs have strong affinity toward sulfur. These toxic chemicals create bonds with S in enzymes, thus inhibiting essential enzyme functioning (Waseem and Arshad 2016).

A brief description of accumulation and physiological role (Ansari et al. 2004) of trace HMs in aquatic species and the potential threats to humans is shown as follows:

#### 1.8.1 Lead (Pb)

Lead is a highly toxic heavy metal; its excessive usage has given rise to major environmental pollution problems and health issues everywhere in the world (Jaishankar et al. 2014). Various sources of environmental lead pollution are as follows: metal plating and finishing, exhaustive emissions from automobiles, pesticides and fertilizers, ores' smelting processes, battery industry effluents, wastes from urban soil, gasoline and dye additives, and chimneys of manufacturing plants (Eick et al. 1999). Humans are exposed through consumption of food and water exposed to lead and also from inhalation (Ferner 2001). Excessive levels of lead cause neurological and physiological effects in humans. The teratogenic effect is particularly a serious consequence of lead toxicity. Lead poisoning inhibits heme synthesis which leads to hematological damage, damage to CNS and PNS, and reproductive, bone, and kidney dysfunction (Ogwuegbu and Muhanga 2005). There is also some evidence pertaining to organolead compounds, regarding their acute toxicities to bottom-dwelling organisms although few studies have stated their chronic effects (Probst 1979).

## 1.8.2 Mercury (Hg)

Hg is studied extensively due to its toxic behavior. High levels of Hg cause acrodynia, also known as pink disease. The sources of mercury are municipal wastewater, mining activities, incineration of hazardous waste, and discharges from industries (Chen et al. 2012). Mercury is present in the environment in three forms: metallic, organic, and inorganic. Each of these forms of Hg has varying toxicity potential and bioavailability (Jaishankar et al. 2014). Mercury when present in aquatic ecosystems like rivers, streams, and seas is being converted into methylmercury by microbes. Organic forms of mercury are extremely toxic to marine life. Marine mammals amass considerable quantity of mercury coming from various food sources short of any harmful effects. Selenium adversely influences toxicity of mercury in organisms like seals, sea lions, and dolphins. Selenium retains stride with the concentration of mercury. The presence of Hg and Se in connective tissues of dolphin liver is actually a consequence of a purifying advancement for the methyl Hg assimilated through their diet (Price et al. 1972).

Mercury salts are exceedingly toxic. Methylmercury is a neurotoxic substance which causes devastation of microtubules and mitochondria and lipid peroxidation. It also causes accretion of neurotoxins like serotonin and glutamate besides aspartate (Patrick 2002). The chief route through which humans are exposed to methyl Hg is intake of marine species having remarkably high concentrations of Hg (Trasande et al. 2005). Methyl Hg is principally toxic. It provokes teratogenic, carcinogenic, and mutagenic alterations in the organism's body. Therefore, methylmercury is the central toxic form of Hg in the environs. The eating of crustaceans as well as fishes poses a chief danger to humans and other animals. The oxidized mercury resides in the brain, while free metal can be eliminated (Rygg 1985; Rule and Alden 1990). The CNS is severely damaged because of inorganic mercury (II).

#### **1.8.3** Cadmium (Cd)

Cadmium was reported to enhance the growth and photosynthesis of phytoplankton at concentrations up to 100 mg L<sup>-1</sup>. Cadmium because of its association with phosphates is supposed to be taken up by phytoplankton, although in two studies, it is being reported that it doesn't show any biomagnification and bioaccumulation. Aquatic organisms have small concentrations of cadmium in the food web, of a few PPM. Cadmium is principally concentrated in kidneys. It is excreted when metalloprotein is formed in the kidneys. Exceeding quantities of cadmium occur in mollusks too. Suzuki in 1979 studied the common limpet along the Bristol Channel-Severn estuary and established a relationship between high levels of Cd and a declined use of glucose. Cd is a by-product of the Zn making, leading the workers exposed to it. Cadmium is also bioaccumulative in nature. Cadmium is responsible for causing the *itai-itai* disease. Cadmium is exposed to man through ingestion and inhalation which ultimately leads to acute and chronic toxicity (Jaishankar et al. 2014). The signs of cadmium poisoning are associated with the kidneys, lungs, and bones. The chronic inhalation of cadmium causes kidney proteinuria (Swarzenski et al. 2000; Szefer 1990).

#### 1.8.4 Arsenic (As)

The chemistry of As is multifarious besides being vital in development of aquatic species. Arsenic is present in various chemical forms: arsenate  $(AsO_3^{4-})$ , arsenite (AsO<sub>3</sub><sup>3-</sup>), methyl arsenic acid [MeAsO(OH)<sub>2</sub>], and dimethyl arsenic acid [Me<sub>2</sub> AsOOH]. AsO $_3^{4-}$  is the main species in the photic zone of water. MeAsO(OH)<sub>2</sub> and Me<sub>2</sub>AsOOH are present in high concentrations (Tay et al. 1992). Algae have extra accruing capability to arsenic than fish, with crustaceans amassing restrained quantity. The arsenic forms are imperative with reference to toxicity. The toxic potential of the arsenic reduces as per the following pattern with As (III) followed by As (V) and then the organoarsenic. It gives the impression that one of the body's resistance counter to arsenic is alkylation, resulting in generation of alkylarsenic (V) compounds: CH<sub>3</sub>AsO(OH)<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>AsO(OH), which are less toxic forms of arsenic, and then these products are excreted from the body (Timmreck and Shook 1992). Acute effects of oral arsenic poisoning are strong abdominal pains, nausea, vomiting, and gastric intestinal complications triggering diarrhea, only to end with coma followed by death. Exposure to arsenic through inhalation causes respiratory effects which comprise of nasal and throat irritation, headache, vertigo, restlessness, and irritability (Rinderhagen et al. 2000; Tsuchiya 1981). As and Se are incompatible in the body and thereby separately stabilize the toxicity of each other. As (III) is deliberated as having the utmost toxicity; arsenate can be troublesome by competing with phosphate, consequently resulting in interruption of oxidative phosphorylation process. Arsenic also impedes the DNA repair mechanism by substituting the phosphorus in DNA (Rinderhagen et al. 2000). It may intermingle with the biosynthesis of porphyrin and distress the white blood cells. Arsenic toxicity has been associated with impacts on the reproductive system such as miscarriages/stillbirths. Hearing impairment is also related with arsenic poisoning. Occurrences like milk adulteration in Japan and discharges from Cu smelters have triggered auditory issues (Stauber and Florence 1990). Arsenic attacks the renal system, predominantly the reabsorption process. It causes destruction to peripheral nervous system (PNS) like peripheral neuritis plus motor sensory paralysis (Tsuchiya 1981).

#### **1.8.5** Barium (Ba)

Barium has no part in biological science. As per *The British Pharmaceutical Codex* (1907), barium chloride ["barii chloridum," BaCl<sub>2</sub>.2H<sub>2</sub>O] has a stimulatory effect on cardiac muscles as well as other muscles. It increases blood pressure by narrowing the blood vessels. It has a tendency to empty intestines, urinary bladder, as well as gall bladder. Its toxic nature has also been verified. Barium sulfate (BaSO<sub>4</sub>) is insoluble and is useful in radiography. All barium combinations should be considered as exceptionally toxic even though there is authorization that its vulnerability is limited and such compounds are not easily accessible to humans. Its toxicity hinges on

the solubility of counterions. The nature of the counterions also plays a significant role. Baritosis is one of the forms of pneumoconiosis that is caused by longtime contact with barite and Ba dust. It has been stated that those workers are more prone to it who are being exposed to crushed and ground insoluble barium salts (US EPA 1992).

## **1.8.6** Zinc (Zn)

Zinc (Zn) is typically existent in plants and animals in concentrations corresponding to iron and generally in far greater concentrations than many other trace elements. Many researches verify that Zn is crucial for bacteria, fungi, and blue-green as well as green algae. Just because Zn isn't considered as highly toxic metal, hence it is being discharged into water bodies in considerable amounts. Limited number of reports shows that some species are susceptible to Zn toxicity at quantities frequently seen in seawater and sediments of estuarine waters. Stauber and Florence (US EPA 1992) observed that the growing of cultural diatoms was restrained by 20 µg L<sup>-1</sup> of Zn. Impacts on fertilization as well as embryonic growth in Baltic spring-spawning herring at low salt levels were perceived at just 5  $\mu$ g L<sup>-1</sup>. On the other hand, many accounts of zinc toxicity were observed in waters having concentrations of Zn beyond 100 µg L<sup>-1</sup>. Zn and Cd toxicity has an inclination to happen in the environs jointly. Zinc has a great number of biological purposes in humans besides being an essential component of more than 100 enzymes responsible for body's metabolism. Zn is involved in the production and functioning of certain hormones. It also executes an imperative part in reproductive as well as sexual maturity. Zinc is also present in the plasma, erythrocytes, leukocytes, and platelets (Van-Loon and Duffy 2000). Commonly found Zn compounds aren't predominantly toxic, while zinc salts can be carcinogenic.

## **1.8.7** Copper (Cu)

Copper (Cu) is a necessary element for some animals. A maximum concentration of it is present in gastropods, decapod, crustaceans, and cephalopods as their blood consists of pigment hemocyanin which holds Cu. Extra Cu is typically deposited in the liver (4800  $\mu$ g g<sup>-1</sup>). Oysters may have similar extraordinary content of Cu that is hoarded typically in the WBCs consisting of 20,000  $\mu$ g g<sup>-1</sup> of Cu and 60,000  $\mu$ g g<sup>-1</sup> of Zn in these blood cells. Cu is among the most toxic metal, following Hg and Ag, to marine life despite many purifying and storing systems. It has been experimentally proved that many aquatic species are negatively affected by Cu levels of 1–10  $\mu$ g L<sup>-1</sup> (Price et al. 1972). Vandecasteele and Block (1993) detected that 2  $\mu$ g L<sup>-1</sup> of Cu had noteworthy impacts on young bay scallops and surf clams. Some bivalves like *Mytilus edulis* were able to tolerate high levels of Cu due to the

presence of Cu-binding metallothioneins (Viarengo et al. 1984). Cu-containing proteins in mammals are cerebrocuprein, ceruloplasmin, erythrocuprein, hemocuprein, etc. Copper enzymes also have the capability to openly utilize molecular oxygen. It has been labelled indispensable for cross-linking of elastin. Cu deficit is responsible for anemia plus disparities in bone development. It is commonly found in populations having malnutrition, also in patients getting whole parental nourishment. The consequence of Cu intake in disproportionate concentrations is hemolysis (splitting of RBC) (Van-Loon and Duffy 2000).

### 1.8.8 Manganese (Mn)

Manganese is among the many vital elements required by plants as well as animals. The biologically functioning form is the  $Mn^{2+}$  ion. It is as an enzyme activator widely distributed all over in the body tissues and fluids. In the human body, its content is projected to be 12–20 mg. It is also involved in mucopolysaccharide breakdown. It is also associated with superoxide dismutase. Pyruvate carboxylase is the single identified manganese-containing metalloprotein. Various experiments have been carried out to determine manganese deficiency in animals although none in humans. Manganese deficiency is responsible for skeletal irregularities. It is minimum toxic trace element to animals. Its prolonged exposure causes manganese poisoning that often occurs in mine workers. Manganese being toxic, when inhaled, causes neurological disorders (Van-Loon and Duffy 2000).

## 1.8.9 Iron (Fe)

Iron is the central constituent of plant and animal life being crucial for their growth and development. In the human body, iron is bound to protein forming complexes as porphyrin or heme compounds, mostly hemoglobin plus myoglobin or as nonheme protein-bound compounds such as ferritin plus transferrin. In humans, Fe binds to oxygen consequently assuring lungs to supply oxygen to the cells. The maximum amount of iron exists in the liver, spleen, kidney, and heart. Fe contamination results in the decrease in the number and abundance of species like periphyton, benthic invertebrates, and fishes (Vuori 1995). The iron precipitation results in substantial impairment to fishes because of clogging action in addition to hindering of respiration (EPA 1993). Iron deficiency is responsible for a number of diseases like anemia, lethargy, headache, as well as anorexia. Children are more susceptible to iron toxicity for the reason that they have maximum exposure to iron-containing products (Albretsen 2006). Excessive intake of soluble iron salts (>0.5 g) results in grave injuries to the digestive track followed by serious problems like hepatitis. Recurrent ingestion of exceedingly abundant quantities of Fe results in hemochromatosis which finally results in liver cirrhosis (Van-Loon and Duffy 2000; Wang et al. 1995).

# 1.9 Trophic Transfer of Heavy Metals

Being persistent pollutants, HMs amass in organisms and are then transmitted from lower trophic level to subsequently higher trophic levels. Food chains and food webs signify association amid organisms; hence all organisms get affected by contamination. The amount of HMs amassed in biota hinges on their rate of absorption and depuration from the body. HMs are transported to living organisms from the abiotic environment (water, sediments, and soils). This can take place either directly or indirectly from its food/prey, e.g., HMs may come in bodies of fishes straight from water and sediments by way of the gills and/or the skin. It can also come from consuming contaminated prey. The concentration of the heavy metal may either rise or fall in subsequent trophic ranks. The buildup of HMs in organisms varies with metal species in consideration and the biological processes established for the homeostasis. It also depends on the detoxification mechanisms. Methylated forms like that of mercury accumulate in biota to larger levels consequently biomagnified due to affinity toward lipids (Fig.1.3). Metallophytes have developed exceptional mechanisms for enduring exceptionally high content of HMs in soil (Ali et al. 2019a, b).

#### 1.10 Factors Regulating HM Bioaccumulation

Many physical, chemical, biological, and environmental factors influence the intake plus withholding of heavy metals by marine organisms (Rashid et al. 2019). Various organisms are evaluated as indicators of heavy metal pollution owing to the fact that the bodily concentration of metal is proportional to the concentration of metal in seawater. For the evaluation of organisms as bioindicators, various factors like the organisms' rate of metal uptake which in turn is dependent on the chemical species of the metal are taken into notice. The chemical factors affecting the rate of metal uptake are pH, temperature, and hardness besides salt levels. HMs normally influence each other and as a result constrain the uptake of another by a specific organism (Ansari et al. 2004). The metal content in an organism depends upon the size of the individual, age, and growth rate. In addition to this, position in the water column also plays important role (Ansari et al. 2004). Furthermore, seasonal variation of the metal concentrations has been observed because of the changes in the organism's weight without any change in the total metal concentration of the organism. In few cases, the metal concentration is dependent on the organism's sex to some extent.



## 1.11 Bioaccumulation of Heavy Metals in Fish

Fishes contaminated by HMs have turned out to be a significant subject all around the globe owing to their antagonistic aftermaths on fish and its consumers (Rahman et al. 2012). Bioaccumulation is regulated by fish age, size, weight, and length, as well as feeding behaviors and body functioning. The environmental factors like content and bioavailability of metals, physicochemical properties of water, and climatic factors also perform a key function. Varying with the structure and functioning of tissues, the degree of heavy metal buildup varies tissue-wise in fishes. In general, organs like gills, liver, and kidneys store much greater concentration of HMs than the skin and muscles because of metal-binding proteins called metallothioneins (MTs) present in these tissues when being exposed to HMs. Fish gills are target tissues for amassing as well as removal of HMs like Ni (Mansouri et al. 2012). Fish muscles don't accumulate HMs in high concentration, but they are important from the viewpoint of human consumption (Khaled 2009). Bioaccumulation of HMs in fish muscles is mostly species specific (Kumar et al. 2010). Elevated level of HMs in aquatic biota poses major health consequences and can result in population decline of aquatic species (Luo et al. 2010). Heavy metals are powerful neurotoxic drivers distressing fish species. The heavy metal interfaces with chemical incitements in fish can interrupt the fish communication with their surroundings (Baatrup 1991). HMs have been connected to fish defects in natural populations. These aberrations have undesirable effects on populace of fish species as these defects impact their morphology, survival, rate of growth, as well as well-being and health. These defects in fish can be explored as exceptional biomarker of heavy metal pollution in the environment (Sfakianakis et al. 2015).

Accretion of toxic HMs in fish has significant environmental and ecological consequences, besides societal concerns; it impacts both humans and aquatic carnivore species feeding on fish (Ali et al. 2017; Ali and Khan 2018a, b, 2019). HMs found in polluted seawater are assimilated in fish, and from there they pass into humans, thereby affecting human health (Dwivedi et al. 2015). In addition, toxic HMs also affect fish health (Javed and Usmani 2015) have reported pollution of river with heavy metals resulting in stress of freshwater fish by weakening it and making it more vulnerable to diseases. Heavy metal pollution is considered among the potential reasons for the decrease in population of freshwater fish and other aquatic organisms (Mehmood et al. 2019). It has been stated that with the rise in pollution levels of Indus, a major river in Pakistan, diversity and abundance of aquatic life were drastically affected (Al-Ghanim et al. 2016).

#### **1.12 Heavy Metal Remediation Techniques**

The remediation method for heavy metals should be cautiously evaluated so that the protection of the biotic and abiotic environment is ensured. All remediation procedures entail treatment of extensive sludge quantity which destroys the natural habitats in addition to being very costly (Nleya et al. 2016) (Fig. 1.4).

#### 1.12.1 Precipitation

Numerous alkaline chemical reagents are commonly used for neutralization of acid mine drainage (AMD). It helps in pH elevation which in turn results in the formation of precipitate, thereby helping in recovering of the metals. Commonly used reagents for the recovery of mineral from AMD are limestone (CaCO<sub>3</sub>), caustic soda (NaOH), soda ash (Na<sub>2</sub>CO<sub>3</sub>), quicklime (CaO), slaked lime (Ca(OH)<sub>2</sub>), and magnesium hydroxide (Mg(OH)<sub>2</sub>) (Masindi et al. 2016). The metal recovery takes place at different pH (Table 1.1). These recycled minerals are vended to metallurgical businesses, thereby offsetting the treatment charges (Nleya et al. 2016).

## 1.12.2 Adsorption

The process of adsorption starts once an adsorbate collects or adheres against adsorbent's surface. Adsorption is much competent and economical method for metal exclusion from aqueous solutions owing to its reversibility besides desorption abilities. Even though it is efficient, this process fails with concentrated solutions. The reason for it is that the adsorbent gets saturated with the adsorbate easily. This method performs well in case of very dilute solutions. It's a tedious task due to the reason that it entails recurrent regeneration in addition to being nonselective (Nleya et al. 2016). Thus adsorption is not effective in metal remediation on a large scale.





Table 1.1 pH for each metal ion at which precipitates formed in AMD

Metal ion	pH	Metal ion	pH	Metal ion	pН
Al <sup>3+</sup>	4.1	Hg <sup>2+</sup>	7.3	Cd <sup>2+</sup>	6.7
Fe <sup>3+</sup>	3.5	Na <sup>+</sup>	6.7	Fe <sup>2+</sup>	5.5
Mn <sup>2+</sup>	8.5	Pb <sup>2+</sup>	6.0	Cu <sup>2+</sup>	5.3
Cr <sup>3+</sup>	5.3	Zn <sup>2+</sup>	7.0		

Masindi et al. (2016)

#### 1.12.3 Ion Exchange

Ion exchange refers to the procedure in which give-and-take of ions takes place among two or more electrolytic solutions. Clay and resins have great cation exchange capability; thus they are frequently employed for metal exchange from aqueous mixtures. The efficacy of this method depends on pH besides temperature. Natural and artificial clays, zeolites, and synthetic resins are utilized for separation and exclusion of metals (Nleya et al. 2016; Masindi 2016).

#### 1.12.4 Biosorption

Biosorption is the process of removing toxins from water systems by making use of biological tools. It includes absorption, adsorption, surface complexation, ion exchange, and precipitation. Biosorbents are advantageous because of their permanence, efficiency, and capability. They are steadily available and can be easily regenerated. However, the process easily reaches a breakthrough, therefore limiting further removal of pollutant (Silvas et al. 2011).

#### 1.12.5 Membrane Technologies

Usage of membrane technologies for the retrieval of AMD is highly resourceful in treating polluted waters having elevated pollutant content. These techniques use the concentration gradient phenomenon or reverse osmosis process. Diverse membranes are used for treating mine waters. These includes ultrafiltration, nano- and micro-separation, reverse osmosis, and particle filtration (Nleya et al. 2016; Buzzi et al. 2013; Park et al. 2015)

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