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Sana Fatima
Gomal Centre of Biochemistry and Biotechnology, Dera Ismail Khan, KPK, Pakistan

Muhammad Muzammal
Gomal Centre of Biochemistry and Biotechnology, Dera Ismail Khan, KPK, Pakistan

Aqsa Rehman
Gomal Centre of Biochemistry and Biotechnology, Dera Ismail Khan, KPK, Pakistan

Saqib Ali Rustam
Faculty of Veterinary and Animal Sciences, Gomal University, Dera Ismail Khan, KPK, Pakistan

Zainab Shehzadi
Department of Zoology, Government College University, Lahore, Punjab, Pakistan

Asmat Mehmood
Department of Zoology, Government College University, Lahore, Punjab, Pakistan

Muhammad Waqar
Atta ur Rehman School of Applied Biosciences NUST, Islamabad, Pakistan

Corresponding Author:
Sana Fatima
Gomal Centre of Biochemistry and Biotechnology, Dera Ismail Khan, KPK, Pakistan

Water pollution of heavy metals and its effects on fishes

Sana Fatima, Muhammad Muzammal, Aqsa Rehman, Saqib Ali Rustam, Zainab Shehzadi, Asmat Mehmood and Muhammad Waqar

Abstract
Water is the most important need; human activities have made it polluted and harmful for life in the water as well as on land. One of the most important pollutants is heavy metals when these HM are present in the water, they can accumulate in fishes and pose a harmful threat to their health. Urbanization and industrialization have led the aquatic system to be polluted by these HM and are affecting the balance of ecosystem and diversity of aquatic life. In water, Zn, Pb, and Ni are the dominant pollutants while Zn is also a major pollutant in sediments. Many hazardous effects are caused by heavy metals on fishes like deformities, metabolic problems, kidney diseases, liver problems, tumors, reproductive loss, and behavioral changes. Fishes are included in the human diet thus these pollutants also indirectly affect human health.

Keywords: Heavy metals, urbanization, industrialization, aquatic life

Introduction
Life cannot exist without water. It's the most important natural resource present and for the welfare of humans, the quality of water is of utmost importance. Even though water is the most important need, human activities have made it polluted and harmful for life in the water as well as on land [1]. The damage comes along with economic growth as a result of industrialization and urbanization. Domestic and anthropogenic activities also lead to polluted water, lowering the quality of water bodies. Water pollution is a universal problem and is seriously affecting aquatic life [2, 3]. One of the most important pollutants is heavy metals (HM).
Heavy metals are those metals that have a higher density (relatively) and a small quantity of them is toxic. Some common heavy metals include As (arsenic), Cr (chromium), Cd (cadmium), Hg (mercury), Tl (thallium) and Pb (lead). Along with these, some trace elements are also included in this list i.e. Zn (zinc), Se (selenium) and Cu (copper). All these elements are important for healthy metabolism but when their concentration increases these elements can also be toxic [4]
When these HM are present in the water, they can accumulate in fishes and pose a harmful threat to their health as well as, fishes are highly demanded as food for a healthy diet. When affected fishes are eaten, these HM enter the human body and can cause damage. HM when present in higher concentration cause a disability of ecosystem, as these metals accumulate in the aquatic animals and enter the food chain causing health problems and even death of some organism [5] .
The toxicity of metals depends on the type of metals. Some metals become toxic when they are soluble in water, they become toxic. Some other metals are poisonous because they are not needed for any biological purpose thus even a small amount becomes toxic. Similarly, the level of toxicity of metals also changes depending on the type of metal. Also, some metals become toxic on change in their oxidation state i.e. chromium which becomes carcinogenic when its oxidation state increase to 4.
HM put a toxic effect by interfering with metabolism and by causing mutagenesis. The toxic effects may lead to a lower level of fitness, low reproductivity and in most lethal cases may lead to the death of the organism.
Industrialization and economic growth go hand in hand but at the same time put a dangerous effect on the ecosystem. We can see these toxic metals producing dangerous effects on the

ecosystem in history i.e. Hg poisoning of water in japan which caused neurotoxicity which was like "*Hunter Russell syndrome"*. Along with these direct effects, the toxicity of HM may also lead to reduced growth of the fetus [6].

Presently, pollution is the biggest problem of the world that is affecting the earth as well as the health of living organisms. As far as the aquatic life is concerned, the main cause is the industrial wastes and heavy metals constitute a major part of industrial waste. Heavy metals can enter the water through the process of smelting, leaching and/or directly through industrial effluents [7].

According to EPA (environmental protection agency) of the USA, handling of toxic material is necessary and precautionary measures should be taken for the disposal of such materials. Often, HM is added to fertilizers absorbed by the plants, polluting the land and entering the food chain cause harmful effect to the health of organism eating those plants [8].

The presence of toxic HM depends on the age, physiological and developmental factors, but still, in human consumption, fishes are the main source of HM like arsenic and mercury. Urbanization and industrialization have led the aquatic system to be polluted by these HM and are affecting the balance of the ecosystem and diversity of aquatic life. Arsenic has been reported as a carcinogen and is present in seawater the most and is reported to be most lethal in +3 oxidation state [9].

Chromium is widely used in the industries of paints and electroplating and enter the aquatic system through industrial effluents. The hexavalent chromium is said to be most toxic for animal's health. Similarly, mercury enters the aquatic system through coal industries in the form of absorbed fumes which highly affect aquatic life [10].

The natural need for heavy metals

Although mostly HM produces dangerous effects on animals, some also are essential for the normal functioning of their bodies thus are present in aquatic bodies naturally but in a specific amount (not toxic) (Table 1). Some of the important roles are:

Vitamin B12 has cobalt; metabolism is regulated by chromium; redox reaction, cartilage formation, respiration is regulated in the presence of copper; peroxidase, catalase, cytochromes, and hemoglobin constitute iron. Similarly, transition metals are also important like:

Manganese plays an important role in urea synthesis, citric acid cycle and saves mitochondria from the effect of free radicals. Nickle is an important constituent of many enzymes and stimulates growth. Molybdenum constitutes the enzymes to produce uric acid and fatty acids. Selenium constitutes an enzyme important for tissue oxidation and cardiomyopathy. Tin constitutes gastric enzymes and plays an important role in growth. Vanadium is important for the mineralization of bones and the metabolism of lipids. Zinc constitute several enzymes that are important for protein synthesis, metabolism, fertility, etc. [11].

Table 1: Heavy metal occurrence in marine and aquatic water naturally [12]

Metal/ Metalloid	Sea water	Fresh water
Aluminum	2	300
Antimony	0.2	0.2
Beryllium	0.006	0.3
Cadmium	0.1	0.1
Chromium	0.3	1.0
Cobalt	0.02	0.2
Copper	0.3	3
Lead	0.03	3
Manganese	0.2	8
Mercury	0.03	0.1
Molybdenum	10	0.5
Nickel	0.6	0.5
Silver	0.04	0.3
Tin	0.004	0.009
Uranium	3	0.4
Vanadium	2.5	0.5
zinc	5	15

HM in water

The major cause of heavy metal pollution is the waste from household landing into the lake water polluting it [13-15]. Zinc is an essential element, but its pollution is calculated to be higher in the lakes and the cause of it is reported to be the presence of particles in the dust that dissolve in water to contaminate it [16]. Along with the dust particles, volcanic eruption, fire, and fertilizers also are involved in zinc contamination. Further, domestic wastes play a major role in water pollution by HM [17].

Another important pollutant is lead which enters the rivers having mining areas in the locality as the fuel used for mining is rich in Pb. Pb also enters the water through the air particulates as well as climatic changes. The presence of humic substances in the soil is also reported to be a major cause of water pollution as it acts as a transporter of heavy metals from the soil into the water [18].

According to the studies, the source of Nickle in the water is due to both point and non-point sources [19], while iron was predominantly, was sourced through the red-ox reactions taking place in the water at sedimentary level [20]. (Table 4)

HM in sediments

The primary cause of HM in sediments is through fertilizers, organic matter and climate change. The most-reported HM in sediments is Zinc and Copper that are essential while non-essential metals are Lead and Cadmium but in a comparatively lower concentration. Studies report zinc to be the major pollutant of the sediments due to increasing industrial waste and anthropogenic activities using zinc as the commercial waste [21].

According to a study report, both essential and non-essential elements were found in the sediments in a wetland of India and the attribution of the pollutants was to anthropogenic activities along with industrial wastes from textile, tanning, dyeing, electroplating, etc. While in another study, major pollutants like, zinc, nickel and chromium were observed in sediments of lakes due to solid waste disposal in the water along with other industrial wastes [22]. (Table 3)

Table 2: Heavy metal concentration in water obtained from different areas [23]

Country	Type of freshwater systems	Heavy metals
Between Peru and Bolivia	Titicaca Lake	Fe 111.6 μg/L Pb 32.39 μg/L Zn 117.32 μg/L
Balkan Peninsula	Lake Skadar	Ni 14.6 μg/L (surface) Ni 12.3 μg/L (bottom)
Ethiopia	Rift Valley Lakes	Cr 27.8 μg/L Cu 15.5 μg/L Ni 22.4 μg/L Zn 48 μg/L
Belgium	Gravel Pit Lake	Fe 53.9 μg/L
Malaysia	Kampar Lake	Zn 43.29 μg/L
Southern Baltic	Coastal Lake	Fe 3.09 mg/dm^{-3} Ni 0.37 mg/dm^{-3} Zn 0.12 mg/dm^{-3}
Finland	Lake Valkea-Kotinen	Zn 6.8 μg/L (median)
America	Louisiana lake, Pontchartrain	Cr 7.0 μg/L Pb 8 μg/L Zn 80 μg/L
Turkey	Cernek Lake, Kızılırmak Delta	Fe 3.77 mg/L (LOQ) Pb 2.25 mg/L (LOQ)
France	Landfill draining pond	Cr 9.70 mg/L Cu 15.10 mg/L Ni 10.61 mg/L Zn 9.90 mg/L
India	Lakes in Bangalore	Pb 0.15 mg/L Ni 0.36 mg/L Zn 0.19 mg/L
Indonesia	Streams/ponds/gold mining	Pb 23 μg/L
China	Dianchi Lake	Fe 1.140 mg/L Pb 1.276 mg/L Zn 0.096 mg/L
Malaysia	Lake Chini	Ni 14.05 mg/L Zn 40.78 mg/L

Table 3: Heavy metal concentration in sediments of different areas [23]

Country	Type of freshwater systems	Heavy metals
China	Aquaculture ponds, mangrove wetland	Cr 29.9 mg/kg Pb 43.1 mg/kg Zn 626 mg/kg
Australia	Illawara Lake	Cu 130 mg/kg Fe 21,600 mg/kg Zn 419 mg/kg
Balkan Peninsula	Lake Skadar	Cr 91.4 mg/kg Cu 36.9 mg/ kg Pb 25.4 mg/kg Ni 126 mg/kg Zn 74.3 mg/kg
China	Taihu Lake	Cr 79.8 mg/kg Cu 37.4 mg/kg Pb 40.2 mg/kg Zn 96.7 mg/kg
Turkey	Cernek Lake	Fe 686.4 mg/kg Ni 217.75 mg/kg
China	Dianchi Lake	Fe 31.805 mg/kg Pb 565 mg/kg Pb 343 mg/kg

Hazard assessment

Although the HM effect depends on the stage, age and other physiological factors of aquatic organisms and for HM itself, it depends on the oxidation state, solubility, and type of complexes formed by them but still poses a major threat to the ecosystem [24-26]. Out of all the HM present in the water, although some are essential for the health of aquatic animals, their exceeding concentrations can be harmful while others which are non-essential can cause harmful effects even when present in small concentration [27, 28]

Chronic Daily Intake (CDI) is the method used by the United States Environmental Protection Agency (USEPA) for the assessment of the risk posed by heavy metals. This method evaluates the bioavailability of HM to asses the toxicity levels. It compares the level of HM with the intake (average) and body weight [29- 31] .

Another parameter used to calculate the health risk is called the Hazard Quotient index (HQ) that is a non-carcinogenic index. This index can be further divided into different levels [32]. Cadmium and lead in fishes, nickel, and lead in snails (edible) and chromium and lead in oysters have a relatively high HQ putting a dangerous threat for the consumers [33- 35].

A similar method is also used called the Risk Quotient (RQ) to check the specificity of the calculated value on environmental targets. This can be done by comparing RQ with PEC (predicted environmental concentration) and PNEC (predicted no-effect concentration) [36].

EF or Enrichment Factor reflects the level of contamination specifically by metals (by man-made intrusions) causing an environmental risk [37]. Based on the level of contamination, EF is also divided into classes. EF calculates the difference between man-made and natural activity causing the enrichment of metals [38].

The Geo-accumulation index is used to calculate the heavy metal contamination in sediments by a comparison between the values obtained now to the values obtained before the industrial activities [39]. These values can be used to check the level of contamination caused by the industries in a specific area [40]. This factor depending on the level of contamination is divided into 7 classes [41, 42].

C_{deg} (Hakanson's contamination degree) [43] is used to calculate the risk by HM by taking samples from at least 5 different places and then comparing it to the value of the metal present in the earth's crust. This factor is divided into 4 classes based on contamination [44].

Risk Index (RI) was first devised by Hakanson based on the level of toxicity caused by the metal but now, this method is not only used to calculate the level of toxicity but can also be used to calculate the combined effect of different HM in an area. This index is calculated by 4 factors i.e. pollutant, the concentration of pollutants, toxicity of pollutant and sensitivity of the water body under process [38, 41]. This index is also divided into further classes depending on the potential risk caused by the pollutant on the ecosystem thus it's also called PER i.e. Potential Ecological Risk [45, 46].

Metal Pollution Index is used to calculate the total metal content present in the sample under process. Similarly, SPI (sediment pollution index) is calculated by adding the EF values along with the level of toxicity produced by them. For individual metal pollutants, the factor used is called Pollution index or PI that is categorized into 6 classes. For the assessment of potential contamination in an area, the Heavy Metal Index is used [47-49].

Another factor to calculate the toxicity of the organisms living in water is BAF i.e. Bioaccumulation factor. It is calculated by comparing the effect of different HM on one tissue or one HM on different tissues of the organism [50, 51].

Effects of HM on fishes

HM can affect the normal functioning, fertility, physiological process and in severe cases may even lead to death [52]. HM can enter fishes through gills, mouth or general body surface but the most common route is through gills by the entrance of contaminated water directly into the body [53, 54] while the rarest route is through the body surface. Through the mouth, entry of HM leads to bioaccumulation through which these HM can enter the food chain [55].

Chromium (on fishes)

HM can accumulate in the body by uptake of water or polluted food intake. Chromium level is increasing in water bodies due to increased anthropogenic activities and range from 1 to 10 ug/L of the contaminated water averagely. Toxicity of chromium in fishes leads to blood-related problems in fishes i.e. anemia, lymphocytosis, eosinophilia with renal and/or bronchial lesions. Chromium poisoning is recorded as the highest in those fish that swim near the effluent disposal [56].

On humans (by eating fish)

Fishes accumulate a large amount of metal as it's at a higher level of the food chain and the level of accumulation depends on the concentration of metal entering the body as compared to concentration leaving the body [57]. Health problems caused by chromium are:

Less immunity, ulcer, stomach problems, skin problems, respiratory problems, mutations in DNA, liver problems, kidney diseases, lung cancer and in most fatal cases even death.

Cadmium (on fishes)

Cadmium is toxic even in trace amounts as it's a non-essential thus is considered public health hazard [58]. It can enter the water bodies through industrial effluents and household waste. Fertilizers used can also leach into water become a source of cadmium accumulation. It affects the reproductive system of fishes and in the long run, maybe the reason for the extinction of species [59]. Cadmium toxicity causes kidney dysfunctions, reproductivity loss, hepatic dysfunctions, tumor production and hypertension in fishes [60].

Effects on humans

The chemical accumulates in the fats of fishes thus when they enter the body of humans, these are protected from the immune system. As cadmium is non-essential thus its more toxic for human health. The health hazards caused by cadmium are:

Vomiting, diarrhea, stomach diseases, bone fractures, DNA mutations, reproductive problems, infertility, nervous system damages, impaired immunity, and cancer [61- 63].

Zinc (on fishes)

Zinc contamination leads to biomagnification when it enters the food chain [64]. Zinc is one of the most important essential elements and at the same time is a leading source of heavy metal pollution/toxicity. Zinc can enter the water bodies through rock weathering or from industrial wastes or other household wastes [65]. But when zinc is present in higher concentration it may cause serious damage to the health of fishes.

Zinc accumulates in gills of fishes which cause respiratory problems that may even lead to death due to deficiency of oxygen. Zinc may also cause physiological changes in the heart of fishes leading to heart failure. Zinc accumulation may also cause behavioral changes. Such fishes show symptoms like restless swimming, air guzzling, dormancy and death [66]. This toxin may also cause pH disturbance, ion regulation and hypoxia [67].

Effect on humans

As zinc is an essential element, a human can tolerate zinc levels to an extent, but higher zinc concentration may lead to serious health problems like:

Skin problems, stomach problems, vomiting, anemia, and nausea. It may even cause damage to pancreatic tissues, arteriosclerosis, and disturbance in the metabolism of proteins. It may also cause respiratory problems if zinc exposure is too long [68].

Lead (on fishes)

Lead becomes toxic when it accumulates in fishes more than the threshold value [69]. Biomagnification causes the toxicity to affect other trophic levels too. Due to concern about human health, lead toxicity is the most studied form of HM pollution. In fishes, it causes problems in the circulatory and nervous system [70, 71].

Effect on humans

The health problems caused by lead in fishes are:

- Effect on organs: damage the liver, bones, kidneys, nerves, brain and reproductive organs.
- Effect on the circulatory system: it causes anemia, high blood pressure, and heart diseases.
- Effect on nervous system: memory loss, behavioral problems, mental retardation, low IQ and damages of nervous system development during pregnancy [72, 73].

Deformities in fishes caused by HM:

Different types of deformities are caused by HM without any specifically known pathway. In *G. affinis* cadmium accumulation leads to disturbance in calcium like hypocalcemia in which more calcium is released from the bones to compensate for the lower level of calcium in the body which in turn causes the deformation of bones. In most cases, the bones affected the most are the bones of the spinal cord which make it too fragile to give support to the body to even move that result in fatal situations to the fishes.

Along with disturbance in Ca level, Cd may also cause bone deformities directly by interacting with the bone's matrix and can cause mineralization or remodeling of bones [74].

HM also affects the developmental processes by affecting the process of mitosis which can lead to delay in the hatching of the fishes. It can also affect the DNA of the fetus and produce deformities in the juveniles. The deformities in juveniles are mostly reported due to the accumulation of cadmium and copper [75].

This reported deformities in the juveniles due to cadmium and copper is studied and is reported to be caused due to metabolic disturbances. In *Perca flavescens* (intoxicated by Cd and Cu) it was observed that oxidative metabolism and mitochondrial enzymatic activity were inhibited directly. [76].

Similarly, in *O. mossambicus* juveniles, this toxification caused the production of metallothionein [77]. In some other studies, it was reported that, as the fishes that are exposed to heavy metals stop feeding, this may result in bone deformities due to nutritional deficiencies [78].

In fishes, it is said that sensitivity is dependent on age i.e. younger the age more will it be sensitive, but in a study, it's reported that in *Gobiocypris rarus* which was exposed to HM like copper, zinc, and cadmium they became less sensitive at embryonic stages rather than the larval stages which contradict the statement provided for the fishes previously.

The notochord is the most important organ in fishes which not only becomes the supporting system of the body but is also responsible for the formation and development of other organs in the body. Thus, those HM that cause deformation in the development of notochord also causes many other skeletal, muscular and neurological deformities in the body. Also, due to abnormalities in muscle formation, many axial structures may be formed abnormally [79].

HM toxicity is also dependent on many environmental factors like the temperature, pH of water, hardness, salt content, solubility, carbon saturation, etc. [80, 81]. The water, which is lower in oxygen concentration, hotter and more acidic tends to cause more toxification of HM in fishes while the presence of more minerals that increase the salinity and hardness of water leads to lower the toxicity of metals [82].

Also, if there is more than one type of heavy metals present in the water, they can interact with each other in such a way that their toxicity may increase or decrease. When the effect of zinc was checked concerning copper on 3 species of fishes (marine) it was reported that for the quality check would be done on any water body, it must take the interacting effect of different metals into account to give a more reliable value of the water condition [83].

Toxicity identification

The toxicity of metals has been studied but now the research on toxicity is shifting more towards the sub-lethal effect of the pollutant rather on the lethal effects as they pose a greater threat toward the contamination due to lower research and literature about it. Although the effects produced by sub-lethal contaminants are not major, they are hard to detect which makes it more dangerous and the consequences of such effects are long term in terms of growth, sustainability, and reproduction. Thus, to get a clear picture of the toxicity of HM, first, the non-lethal effect should be omitted until adulthood so that they only affect to be calculated on adult fishes are only the effects produced by lethal HM [84] .

The presence of deformities in wild fishes may indicate as an indicator of the presence of contamination in the water and specificity of type of heavy metals can be indicated by checking the deformities type in the wild fishes [85-87]. Similarly, sub-lethal effects can indicate the level of contamination in a specific water body and this, in turn, indicate the water pollution caused by different contaminants (heavy metals). Also, to check the water quality, tolerant fishes can be used to check the effect of different pollutants which can show the relationship between HM and deformities [87-89]

Conclusion

The presence of heavy metal has been studied all over the world and is reported to be hazardous to aquatic life and in turn for human health. Many pollutants are present in the water like zinc, nickel, lead, cadmium, etc. that enter the water through point as well as non-point sources i.e. industrial wastes, agricultural wastes, domestic wastes, etc. and causes damage. This pollutant efflux should be prevented by filtering the waste materials to lower water pollution and maintaining balance in the ecosystem. Identification of water pollution should be measured through chemical as well as biological indicators which will be the most important step towards a better environment.

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