



## Contamination by heavy metals of fishery products in Morocco

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### Abstract

The Moroccan coast corresponds to a space of intense economic activities (industrial, agricultural, domestic etc..), and thus constitutes the receptacle of significant quantities of substances of natural or anthropic origin, many of which possess toxic properties. Heavy metals are pollutants whose harmfulness is related to their persistence and their speciation. They are poorly metabolized, so they can be transferred to the food web and accumulate in living matter. In the present study we have given an idea of the state of contamination by heavy metals in Morocco as well as their mode of transport, their accumulation in fish products, and their effects on the human health and the environment.

*Keywords:* Heavy metals, contamination, fishery products, Mediterranean Sea, Atlantic coast.

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### Introduction

The populations are led to consume more seafood. In order to diversify their diet. They represent good sources of proteins and minerals beneficial to health. Such as essential fatty acids and mainly long-chain polyunsaturated fatty acids of the omega-3 family, proteins, vitamins A, D and E and mineral elements. Indeed, a serving of 150 g of fish can provide, approximately, from 50 to 60 percent of the daily protein requirements of an adult [1].

Numerous studies have shown the potential action of fish consumption for the prevention of cardiovascular and coronary diseases [2, 3], strokes [4], certain cancers [5, 6], depression, and certain neurodegenerative diseases [7].

The universal problem is the environmental pollution and most important pollutants are the heavy metals in aquatic network because of their toxicity, accumulation and bio-magnification by marine creatures. Domestic, industrial and anthropogenic activities may broadly become the source of natural aquatic systems contamination of heavy metals [8,9]. The pollution caused by heavy metals might have. The heavy metal pollution has dreadful effects on the environmental equilibrium and a variety of aquatic entities [10, 11]. In the list of animal species, detrimental effects of these pollutants, can never be negligible for fishes [12,13,14]. Fishing is a also general pastime [15,16,17] including in urban areas [18].

However, fish are also sometimes a major contributor to exposure to certain environmental contaminants [19, 20]. Metallic trace elements (ETM), such as, cadmium lead and persistent organic pollutants (Dioxins, Polychlorobiphenyls, Polybromodiphenylethers, etc.) represent a group of toxic substances that accumulate in the tissues of fish and transfer along from the food chain to humans [1].

The successive accidents of human poisoning with cadmium and lead, highlighted in industrialized countries, have placed the subject of environmental pollution as one of the major challenges of our time. The industrial and technological revolution of the 19th century was accompanied by a notable increase in releases into the environment by humans of these natural or synthetic substances which have direct or indirect effects on human and environmental health. Recent studies relate to an intoxication which took place in an island of Southeast Asia (Chichigalpa), where almost 200 000 people, mainly farmers, would suffer from chronic renal failure. The measurements revealed significantly higher levels of cadmium and pesticides in the urine of sick people [21].

In Thiaroye on the Dakar Sea, in Senegal in August 2008, eighteen unexplained deaths of children living in a village were reported as a result of lead poisoning [22].

In Morocco, we have not found enough studies on the heavy metal content in certain species of fish that are consumed a lot by Moroccans. And that the heavy metals often sought are lead and cadmium while there are other metals which are toxic apart from these metals. Therefore, we saw it necessary to provide more data on the concentrations of these metals in the edible tissues of some fish species, in order to better assess the risk associated with the consumption of this food stuff.

### 1. Pollution of marine waters in Morocco

The Moroccan coast extends over 2934 km of Atlantic coast and 512 km of Mediterranean coast.

This coastal zone concentrates the main part of the national socio-economic activities, which it is about industry, fishing, tourism, port activity or navigation. The Atlantic coast is home to more than 61% of the urban population of the large cities, 80% of the permanent workforce of industrial units, 35% of tourist capacity and 92% of maritime traffic. Needless to say, this is an extremely rich environmental heritage in terms of flora, fauna, natural sites and wetlands. The maritime transport activity of potentially polluting products, such as hydrocarbons or chemicals, exposes Morocco to high risks of accidental marine pollution. [23]. Morocco has abundant natural resources, particularly marine resources, which have been significantly affected in recent years by economic and demographic pressure, rapid urbanization and their indiscriminate exploitation. The Moroccan coast has been subjected in an exceptional way to the growth of urban agglomerations and to the negative effect of various industrial, port and tourist activities, not to mention the contributions of watersheds, wadis and rivers that dump their waste water and the waste generated by cities and their peripheries. As for the pollution of the sea, it is mainly of land-based origin: domestic and industrial wastewater, solid waste discharges and solid transport resulting from erosion or land reclamation, river or agricultural drainage. As for the sources of pollution at sea are regular discharges from ships, such as waste and ballast, as well as accidental or deliberate discharges. The areas of the Moroccan Mediterranean coast are subject to four types of pollution: municipal and industrial wastewater; agricultural run-off and leaching; oil and chemical waste discharged from ships; and the disposal of solid waste, especially plastics. In addition, these areas are also suffered from marine pollution generated by maritime transport, in particular by oil tankers and tankers carrying toxic and dangerous products at the level of the Strait of Gibraltar and off the Moroccan coast [23]. A study published in 2009 by the Department of Spatial Planning and the Environment revealed the importance of industrial pollution. Out of 220 industrial activities and 6287 production units, 81 activities were deemed to be significantly polluting: The agri- food industries (68% of toxic and organic discharges) followed by far by chemistry-parachimistry (20%) and the textile industries and leather (10%). The study found that this is structural pollution in that it is part of the manufacturing processes of these industries. This urban industrial pollution is concentrated in particular on the Atlantic coast. In fact, the Atlantic coastal basin with the Greater Casablanca achieves for 35% of the total polluting discharges, followed by the SEBOU wadi (the Kenitra region) with 28% and the Tangiers with 11%. However, it should be noted that Moroccan cement factories have made an effort to comply with environmental standards, in particular the ISO 14000 standard, which is the world reference in this area. This pollution of the Moroccan coast is the result of an interaction between coastal

uses, activities and resources. Thus, activities produce negative effects on resources and, in turn, degraded resources limit activities (e.g. fishing). These interactions have been identified in the Moroccan Mediterranean regions. For this reason, Morocco is participating in a programme to monitor the degree of pollution of its Mediterranean coasts within the framework of the Mediterranean Action Plan (MAP) in implementation of the Barcelona Convention of 1976 and its protocols, which Morocco has ratified. This monitoring is organized according to the potential sources of pollution of certain reference coastal areas or bathing areas for example [23].

## **2. Types of pollutants**

### **2.1 Inorganic pollutants**

Industrial, agricultural and domestic wastes contribute to environmental pollution, which cause adverse harm to human and animal health. From such sources, inorganic pollutants are released. Inorganic pollutants are usually substances of mineral origin, with metals, salts and minerals being examples [24]. Studies have reported inorganic pollutants as material found naturally but have been altered by human production to increase their number in the environment. Inorganic substances enter the environment through different anthropogenic activities such as mine drain-age, smelting, metallurgical and chemical processes, as well as natural processes. These pollutants are toxic due to the accumulation in the food chains [25].

### **2.2 Organic pollutants**

Organic pollution can be briefly defined as biodegradable contaminants in an environment. These sources of pollution are naturally found and caused by the environment, but anthropogenic activity has also been contributing to their intensive production to meet the human needs. Some of the common organic pollutants which have been noted to be of special concern are human waste, food waste, polychlorinated biphenyls (PCBs), polybrominated diphenylethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), pesticides, petroleum and organochlorine pesticides (OCPs) [26]. Organic pollutants have gained attention as they have become a major problem in the environment. Properties of organic pollutants, amongst others, such as high lipid solubility, stability, lipophilicity and hydrophobicity have recently made organic pollutants termed persistent. These properties give organic pollutants the ability to easily bioaccumulate in the different spheres of the environment, thus causing toxicological effects [27, 28].

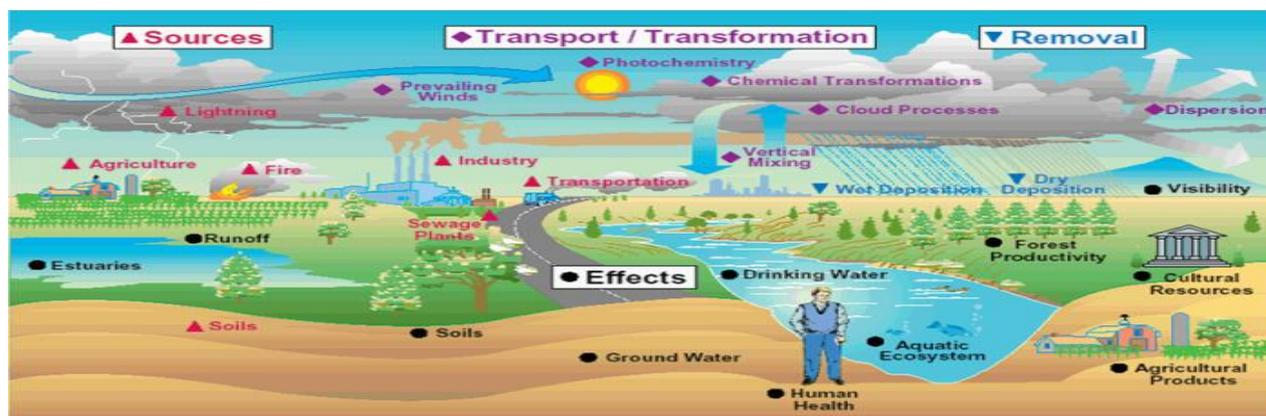
### **2.3 Biological pollutants**

Biological pollutants are described as pollutants which exist as a result of humanity's actions and impact

on the quality of aquatic and terrestrial environment. This type of pollutants includes bacteria, viruses, moulds, mildew, animal dander and cat saliva, house dust, mites, cockroaches and pollen. [29].

### 3. Process of pollutant arrival in the aquatic environment:

Pollutants in the aquatic environment can follow different pathways, of varying lengths (Figure 1). Some pollutants are broken down very quickly by chemical reactions, under the effect of light, or through the intervention of microorganisms (biodegradation). Other pollutants are persistent and contaminate the aquatic environment for a long time, either by remaining in the water and especially in the sediments, or by passing through living organisms, and in some cases by passing through food chains (bioaccumulation). The self-purification capacity of an ecosystem depends on its physical structure, its biological composition (number of species present) and its functioning. According to LACAZE, there are four main modes of transport of pollutants to the sea:- Runoff: Natural or synthetic substances deposited on the ground are carried away by rainwater, and transported to the marine environment by rivers and streams. - Atmospheric fallout: Some substances can be transported over considerable distances and fall back to the land or the sea with precipitation.



**Figure 1:** Pollution sources, transport, transformations, removal and effects [31]

- Direct discharges: All pollutants are likely to enter the marine environment, either directly or via rivers. They are also very unlikely to leave them. Seas and oceans are universal collectors of all pollutants. - Discharges by emitters: Domestic and industrial wastewater, collected and treated in wastewater treatment plants, is discharged into rivers or seas. These treatments, far from being perfect, do not eliminate all toxic substances [30].

### 4. Heavy metals in the marine environment:

The marine environment, a particularly rich biotope, is characterized both by a remarkable stability of its fundamental properties and a great variability of its micro-constituents. Sea water contains in solution

combinations of all chemical elements but only some of them. These twelve major elements account for 99.4% of the total mass of the earth's crust (O, Si, Al, Fe, Ca, Na, K, Mg, Ti, H, P and Mn in order of abundance). Trace elements, numbering 68, represent only 0.6% of the total by mass and are at concentrations lower than  $10^{-6}$ M in seawater [32, 33].

These elements are involved in chemical reactions and contribute to the equilibrium of the marine environment. However, the input of metallic contaminants through industrial effluents and the atmosphere, rivers and their estuaries can change the composition of seawater which can become toxic to plants and animals.

The study of the interaction between contaminants and biological barriers is of considerable interest for the understanding of ecotoxicological phenomena, particularly bioaccumulation and transfers through trophic chains. The processes involved are very complex and are influenced by the contaminant (size of the molecule, chemical speciation, etc.), the receiving organism (membrane properties, chemical composition, active processes, etc.) and the intra- and extracellular environment (temperature, pH, etc.) [32]. Various terms are used to refer to the processes that define the fate of trace metal elements in the aquatic environment. Bioaccumulation is the process of assimilation and concentration of heavy metals in the body. The process occurs in three stages [32]: assimilation, bioaccumulation by the individual, or bioconcentration, and bioaccumulation between individuals, or biomagnification.

#### 4.1. Assimilation

There are two main routes of exposure to pollutants: the external route, by contact (via air or water...) which causes adsorption (the toxic substance remains on the surface), and the internal route by assimilation or absorption. Not all absorption is necessarily dangerous. On the one hand, everything obviously depends on the concentrations of the pollutant. On the other hand, only the soluble fraction - 95% bioavailable - of the metal should be considered; the other, insoluble, poorly bioavailable fraction is eliminated by different routes: solid route (faeces), liquid route (urine), cutaneous route (sweat, etc.). The soluble, bioavailable, assimilable part is concentrated in certain organs. This is called organotropism. This "receptivity" is due either to a particular function (e.g. the liver, the main site of metabolism, i.e. the transformation of matter, or the kidney, the site of excretion), or to the physicochemical composition of the organ, which favours the storage of the contaminant (e.g. calcium/lead in the bones) or allows accumulation (e.g. organs rich in lipids will strongly accumulate organic pollutants). There are also differences between metals. Cadmium concentrates almost exclusively in the digestive tract, liver and kidneys. Lead also diffuses in the skin, muscles and spine. Mercury, in its organic form, diffuses into the nervous system and the foetus [33].

**4.2 Bioaccumulation by the individual or bioconcentration:** Bioconcentration is a special case of bioaccumulation. It is defined as the process by which a substance (or element) is present in a living organism at a concentration higher than that of its surrounding environment. It is therefore the direct increase in the concentration of a contaminant when it passes from water to an aquatic organism [34].

This process of bioaccumulation is expressed as a ratio between the concentration of the compound under study in the environment and the concentration in the organism. This ratio is known as the bioconcentration factor (BCF). Living organisms concentrate metals much more than water and air.

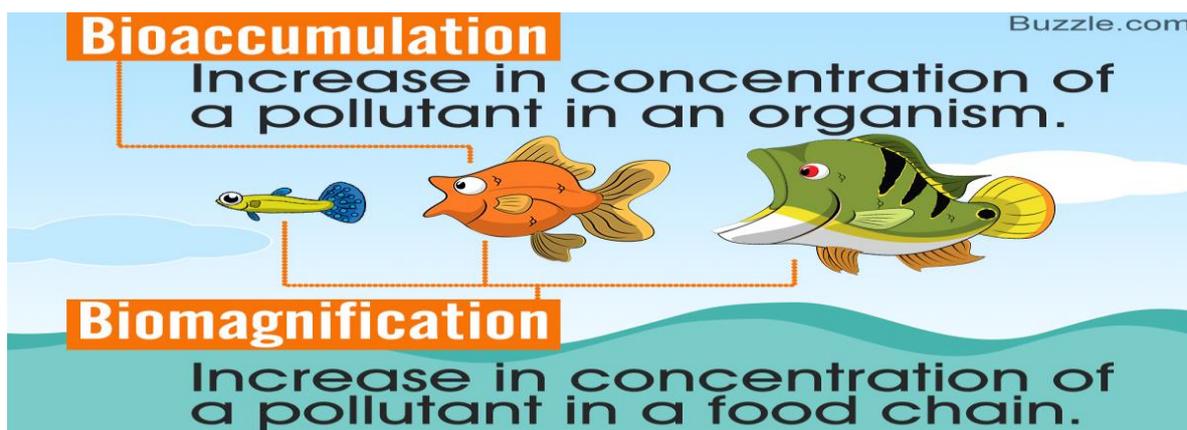
The bioconcentration factor is expressed by the relationship:  $BCF = \text{concentration of the pollutant in the fish} / \text{concentration of the pollutant in the lake ecosystem}$ . A factor greater than 1 indicates bioaccumulation, according to these authors. For example: Mussels are bioaccumulative species that can bioconcentrate molecules from the environment to levels several hundred thousand times higher than those measured in the water. Fungi do the same for many heavy metals in soil, and lichens or mosses can bioconcentrate air pollutants (metallic trace elements such as mercury, cadmium or lead) [35].

#### **4.3 Bioaccumulation between individuals: biomagnification**

Transfers of metals between individuals follow a classic process known as trophic transfer. The pollutant, present in algae and microorganisms, is ingested by a herbivore, itself prey for a carnivore, itself prey for a super carnivore, animal or human. At the end of the chain, therefore, we find ourselves with a final consumer who has bioaccumulated the soluble forms of metals. Concentrations increase as one progresses through the trophic chain. This is the case for lead and especially mercury in the methylated form. Mercury accumulates at each stage and is concentrated at the end of the food chain, particularly in large piscivorous fish. This phenomenon is called "biomagnification" [36].

#### **5. Effects of heavy metals on fishes**

The toxic effects of heavy metals can affect the individual growth rates, physiological functions, mortality and reproduction in fish [37]. Heavy metals enter in fish bodies by three possible ways: by gills, by digestive track and body surface.



**Figure 2:** Bioaccumulation between individuals: biomagnification

The gills are considered as the significant site for direct uptake of metals from the water [38, 39], though the body surface is normally estimated to take minor part in uptake of heavy metals in fish [40]. Heavy metal accumulation can also be caused by the food source, possibly leading to bio-magnification, the augmentation of toxins up the food chain [41]. The periodic difference of heavy metals based on the data of two consecutive years and samples gathered from the fish farm exposed the following result: summer > autumn > winter > spring. As a human food, Fish are considered as an excellent source of polyunsaturated fatty acids (predominantly omega-3 fatty acids), protein, Zn, iron and calcium [42]. Seafood will be an even more important and safe source of food in future for protein and fatty acids for human intake and products made from aquaculture [43]. Different factors that are considered to be critical are size, developmental stage and salinity in heavy metal toxicity to marine and estuarine organisms [44]. Affected organisms show response to heavy metals by accumulating in their bodies or by shifting to the next trophic level of the food chain [45].

### Effects of chromium on fish

Heavy metals accumulated in fish either from the surrounding water or by ingestion of food in environment [46]. Due to anthropogenic activities natural water is being contaminated by this metal. The chromium concentration in rivers and lakes stated to range between 1 to 10 ug/L and EPA recommendation for permissible level are 50 to 100 ug Cr/L for protection of human health and aquatic life respectively. Some species of fishes have poisonous effect of chromium as echoed in the blood changes such as anemia, eosinophilia and lymphocytosis, bronchial and renal lesions. Chromium known for its lesser accumulation in fish bodies while the higher concentrations of Cr damages the gills of fish swimming near point of Cr disposal [47].

### **Effect of chromium on humans by fish intake**

Fish being at the higher level of the food chain accumulate large quantities of metals and the accumulation depends upon the intake and elimination from the body [48]. Cr (VI) is harmful to human health, mainly for those who work in textile and steel industry. The tobacco smokers also have higher possibility of disclosure to Cr. Chromium (VI) can cause many health effects. Chromium in leather products can cause skin rash like allergic reactions. After breathing in Cr can cause nose irritations and nose bleeds [48].

### **Effects of cadmium on fish**

Cadmium is the non-essential and most toxic heavy metal which is widely distributed in the aquatic environment and earth's crust. In the list of heavy metals such as lead, mercury and cadmium are considered to cause public health hazards [49]. Burning of fossil fuels and municipal waste are known to be largest sources of cadmium release to the environment (such as coal or oil) [50].

Cadmium may also enter into the atmosphere from zinc, lead or copper smelter [51]. It can enter into the fresh water by disposal of industrial and household waste. Fertilizers often contain some cadmium. Reproduction rate of aquatic organisms may also be affected due to Exposure to heavy metals and can lead to a gradual extinction of their generations in polluted waters [52]. For example, Cd and mercury (Hg) damage the kidney and produced signs of chronic toxicity, including impaired reproductive capacity and kidney function, tumors, hypertension and hepatic dysfunction [53]. Fish creates major sources of human beings food which is protein. Fishes are major part of the human diet and it is therefore not surprising that numerous studies have been carried out on metal pollution in different species of edible fish [54, 55, 56]. The nutritive need of different tissues of fish depends on their biochemical configuration like mineral contents, amino acids, protein and vitamins, etc. The sub lethal concentration of Cd has showed deviations on the electrophoretic arrangements of protein segments in gills and muscle *O.mossambicus*.

### **Health effects of cadmium in humans by intake of fish**

Unfortunately, the chemical contaminants are stored within the lipid component of the fish [57] so they are well protected when entering the human body. Wild fish from certain polluted areas may be highly contaminated [58]. Metals such as cadmium, mercury, arsenic and lead are non-essential and therefore have toxic effects on living organisms [59, 60, 61]. These heavy metals accumulate in tissues and body of aquatic organisms in higher concentration than concentrations in water and biomagnified in food chain that cause physiological damages at higher trophic levels and in human consumers.

Human being takes Cd mainly through food. Food materials contains higher Cd can significantly increase the Cd concentration in human bodies. The food materials that contain higher Cd are; fish liver, shellfish, mushrooms, dried seaweed etc. In start Cd transported to liver through the blood where it bond to proteins to form complexes that are transported to kidneys where it harms the purifying mechanisms. In results, this causes the excretion of sugars and essential proteins from the body and further damage kidneys. It takes time before Cd that accumulated in kidneys and excreted from human body.

### **Effects of Zinc on Fish**

Zinc can accumulate in the bodies of fish, when they live in Zn contaminated water courses. When zinc enters into the bodies of these fishes, it results in bio magnify up the food chain. The Zn concentrations in fish tissue decreased meaningfully with increasing length of the fish, is regarded as a controversial subject [42], Zinc, an essential element, is one of the most common heavy metal pollutants. The sources of zinc and other heavy metals in natural waters may be from geological rock weathering or from human activities such as industrial and domestic wastes water discharges and animals where it forms constituent functions in maintaining cytoplasmic veracity [62]. However, at higher concentrations, Zn produced adverse effects in fish by structural damages, which affects the growth, improvement and survival of fish. Zinc accumulates in the gills of fish and this designates a depressing effect on tissue respiration leading to hypoxia which results in death. Zinc pollution also tempts changes in ventilator and heart physiology [63]. Sub-lethal levels of zinc have been known to unfavorably affect hatchability, existence and hematological strictures of fish. Zinc could cause sub-acute effects that change fish behaviors. Such observed behaviors include deficiency of balance since most fins are stationary in the affected fish, restless swimming, air guzzling, periods of dormancy and death [64]. The Zn danger is taken as very serious because of its almost unlimited persistence in the environment because it just transformed from one oxidation state or organic complex to another and cannot be destroyed biologically. Zinc is a potential toxicant to fish [65] which causes disturbances of acid-base and ion regulation, disruption of gill tissue and hypoxia [66].

### **Effects of Zinc on Humans by Intake of Fish**

Its need of time to define the concentrations of heavy metals in commercial fish and shrimps in order to determine the possible risk of human consumption. Accumulation of heavy metals in tissues mainly depends upon concentration of metals in water and exposure period; although some other environmental factors such as salinity, pH, hardness and temperature play significant roles in metal accumulation [67].

Zinc is unique element that is little essential for human health. When people exposed to little Zn they can experience decrease in sense of taste and smell, loss of appetite, slow wound healing and skin sores while Zn deficiencies can even cause birth defects. Although humans' beings can manage large concentrations of Zn, too much Zn can cause prominent health problems such as skin annoyances, such as stomach cramps, anemia, vomiting and nausea. High levels of Zn damages the pancreas and disturb the protein metabolism, and cause arteriosclerosis. Extensive exposure to Zn chloride can cause respiratory disorders. However, it is worth mentioning that some of the researchers are of the view that adverse effects of the fish are neutralized in the process of cooking.

### Effects of Lead in Fish

When accumulation reaches a substantially high level, accumulated heavy metals in the tissues of aquatic animals and may become toxic [68]. Aquatic organisms exposed to a higher concentration of heavy metals in water may take up substantial quantities of these metals. Bio-magnification of a pollutant may lead to toxic levels in species high up in the trophic chain and in freshwater systems. Lead (Pb) is as a potent environmental pollutant. Lead toxicity has become very important due to its great concern for human health [69, 70, 71]. Fish are usually among the top consumers [72]. Fish and people are primarily exposed to Pb by food ingestion and breathing. Lead accumulates in the muscles, bones, blood and fat. Newborns and young children are especially delicate to even low levels of lead [73].

- **Effects organs** : Pb severely damage to liver, kidneys, brain, nerves and other organs. Exposure to Pb may also lead to reproductive disorders osteoporosis (brittle bone disease).
- **Affects the blood and heart** : Pb exposure causes increases in heart disease, high blood pressure, especially in men. Pb also causes anemia.
- **Affects the nerves and brain** : Extensive exposure to Pb causes memory problems appropriations, behavioral disorders, mental retardation while lesser levels of Pb damage the nerves and brain in fetuses and young children, resulting in lowered IQ and learning deficits.
- **Effects on Fish** : Lead enters in water systems through runoff, industrial and sewage waste streams. Increasing levels of Pb in the water can cause generative damage in some aquatic life and cause blood and nervous changes in animals and fish and other [74, 75,76].

## Conclusion

The heavy metals are most toxic to all human beings, fishes and environment. The excess levels of heavy metals cause severe toxicity. Though some heavy metals are essential for Animals, plants and several other organisms, all heavy metals exhibit their toxic effects via metabolic interference and mutagenesis. The Pb cause severe toxicity in all. Fishes are not the exception and they may also be highly polluted with heavy metals, leading to serious problems and ill-effects. The heavy metals can have toxic effects on different organs. They can enter into the water via drainage, atmosphere, soil erosion and all human activities by different ways. With increasing heavy metals in the environment, these elements enter the biogeochemical cycle leading to toxicity in animals, including fishes. For this reason, we saw it necessary to provide more data on the concentrations of these metals in the edible tissues of some fish species, in order to better assess the risk associated with the consumption of this food product.

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