

## **Analysis of Trace Metal Bioaccumulation in Fish and Man; Health Risk Impact**

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**ABSTRACT:** *Trace metals occur during natural processes and are also obtained during anthropogenic activities. Streams, lakes and rivers surrounded by farmlands engaged in the use of Trace metal-enriched fertilizers have shown a possible and positive correlation to the rise of Trace metals in the use of chemical, organic and water-soluble fertilizers for a long period. there is a tendency for high correlations of trace metals in source waters. Furthermore, the increasing level of trace metals in fish is alarming and has spurred scientists to make research on the dangers caused by the trace metals resulting in trace metal accumulation and bioaccumulation of life cells. This study aims at assessing the possible sources of trace metals in the aquatic environment, the impact of Trace metals in the aquatic environment, their bioaccumulation in fish and human health risk impact, negative effects in fish have been attributed to the accumulation of trace metals such as irritation of the gastrointestinal mucosa, nephritis, necrosis, neurological and behavioural disorders and death amongst others). The ingestion, absorption and uptake of trace metals in fish are usually toxic and result in harmful damage to the fish and fish life. Since most of the metals taken up are non-biodegradable, such metals can bioaccumulate and bio-magnify. Over time, the accumulated metals affect the growth and development stages of fish from the production of viable eggs, hatchability laval, fingerlings and juvenile life stages. This is so because the early life stages are more sensitive than during maturing and adulthood. In conclusion, negative results of the presence of trace metals and the effect of bioaccumulation and bio-magnification have been reviewed in this paper. This study recommends that the proper assessment and treatment of all forms of wastewater, agricultural waste, sewage, and industrial effluents be carried out before their discharge into the environment.*

**KEYWORDS:** bioaccumulation, death, environment and health status, natural pollution, toxic effect

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### **INTRODUCTION**

Trace metals (TM) are metals which have a density of above 5 mg·cm<sup>-3</sup> and negatively affect life in any form. They are harmful when they exceed threshold limits [1]. TM occur during

natural processes such as erosion, volcanism and weathering. TM is also obtained during anthropogenic activities that take place in the; industry, mining, metal smelting, oil refining, agriculture and fertilization and drainage [2].

Trace metal pollution in rivers, streams and lakes is of severe threat to fisheries and public water supplies. [3, 4,5]. In the ecosystem, trace metals are found in the aquatic environment from contamination by deposits of trace metals from industrial, agricultural waste and by-products and domestic waste and by-products. When TM become highly concentrated in a medium or niche such as air, water and soil such medium becomes toxic and then accumulates in the environment because they do not degrade. Gradual, persistent and increasing accumulation of these Trace, toxic metals can lead to devastating effects on life and aquatic biomes, fish life, diversity and conservation [5,6,81,82]. Living organisms especially humans become contaminated by association with aquatic systems polluted by organic and inorganic heavy metals, also from the consumption of foods and diets made from aqua produce. Fish is one of the essential foods needed by humans for nutrition, providing protein, as well as essential minerals and vitamins, again, a healthy fatty acid with low cholesterol level that is healthy for consumption and capable of reducing diseases of the heart, and stroke [4]. The role of Fisheries in the ecosystem serving as food along the food chain, hence their presence and importance cannot be overlooked as the trace metal accrued in fish results in an impact on human health [8,6,82]

Over the years the rate at which trace metal deposits are observed in fish is alarming and has spurred scientists to make research into the dangers caused by Trace metals resulting in trace metal accumulation and bioaccumulation to living cells. Trace metals are easily accumulated in fishes because they are readily taken up by body parts of fishes such as body surface, gills, digestive tract, liver and muscles. The highest point of TM levels of concentration in the organs of organisms are often the gills than the liver and then the muscle shows the lowest concentration levels. However, the muscles are the most source of Trace metal intake to the body since the muscles are the largest consumed parts of the body hence the ability to cause a negative impact towards health [9].

Caution must be taken to assess the levels of Trace metals for consumption [1,8,5].

Trace metals include Chromium (Cr) Cadmium (Cd), Arsenic (As) Lead (Pb), Zinc (Zn), Nickel (Ni), Mercury (Ag), Selenium (Se) and Copper (Cu) hence their presence in the aquatic habitat are highly toxic to fishes and shellfishes. Freshwater fishes are more prone to heavy metal pollution because of their higher ability to bioaccumulate and thus are easily exposed and vulnerable [10,11]. This study aims at assessing the possible sources of trace metals in the aquatic environment, the impact of trace metals in an aquatic environment, the results of such accumulation of TM (bioaccumulation) and the resulting impact on human health.

## **MATERIALS AND METHOD**

This paper reviews the effects of bioaccumulation of trace metals in fish and humans. Information used was obtained from results and reports from various authors and the findings

from already published papers carefully assessed. Efforts were made to emphasize the various reasons responsible for the observed results.

## RESULTS

Trace metals become available in the environment from various sources and processes:

Natural processes: Research has revealed that under specific environmental conditions and numerous processes, heavy metals are released naturally into the environment. Such of processes include erosion, volcanic eruption, weathering, rock weathering, sea-salt sprays, forest fires, biogenic sources and wind-borne soil particles. During natural weathering, heavy metals in the form of hydroxides, oxides, sulphides, sulphates, phosphates, silicates and organic compounds of varying amounts are deposited in the environment [12]. These TMs are substances that occur naturally in the environment but in trace amounts with no important biological role to play in human existence; causing many toxic effects that lead to malfunctioning of the body systems and disruption of the metabolic process [13].

Anthropogenic processes: Industries, aquacultural and agricultural practices, wastewater, mining and metallurgical processes, and runoffs also lead to the release of pollutants to different environmental compartments. Anthropogenic processes of heavy metals are recorded to go beyond natural fluxes for some metals. HMS from industrial activities and location are equally blown as dust by wind, some are emitted from the combustion of Hydrocarbons and released as automobile exhaust to release lead; smelting releases smelting which releases arsenic, copper and zinc; insecticides which release arsenic and burning of fossil fuels which release nickel, vanadium, mercury, selenium and tin. Human activities have been found to contribute more to environmental pollution due to the everyday manufacturing of goods to meet the demands of the large population [12]. Table 1 shows the standard residue limit for heavy metals in soil.

Table 1. WHO Permissible limits for heavy metals in soil

Elements	*Target value of soil (mg/kg)
Cd	0.8
Zn	50
Cu	36
Cr	100
Pb	85
Ni	35

\* Target values are specified to indicate desirable maximum levels of elements in unpolluted soils

Source: [14] WHO permissible limits for heavy metals in plant and soil.

Above this limit, the environment could be said to undergo pollution. This report from WHO guides nations on the limits with which heavy metal deposition should not exceed. Table 2

**Table 2:** International guidelines for heavy metals in fish, sediment and water

Heavy Metals	Fish		Sediment		Water	
	Means of total concentration in present study	Maximum limit WHO/ FEPA (mg/kg)	Means of total concentration in present study	Maximum Limit WHO/ FEPA(mg/kg)	Means of total concentration in present study	Maximum Limit WHO/ FEPA (mg/L)
Zn	2.917	30	16.063	0.0123	0.635	3.000
Cu	0.218	3.0	0.669	0.025	0.020	1.000
Mn	2.414	0.5	17.453	0.030	0.293	0.050
Fe	1.752	0.5	3.5	0.030	0.153	0.300
Pb	0.113	2.0	2.063	0.040	0.038	0.010
Cd	2.288	0.5	2.630	0.006	0.438	0.003

Source: [87].

Trace metals are introduced into the aquatic environment by activities from the use of: **Agricultural sector** and **Pesticides**. Pesticides are all chemicals and substances that are used to kill or control pest and diseases which includes herbicides (weed), insecticides (insects), rodenticides (rodents), fungicides (fungi), nematocides (nematodes) or in disease control programs to safeguard humans from vector-borne diseases. In addition to the aforementioned are; pet shampoos, skin care and tick sprays for livestock [15]. Pesticides contain numerous chemical composition characteristics such as organochlorine organophosphorus (OPs), carbonates, pyrethroids, neonicotinoids and sulfanilic, carbamic acid, pheylypyrazole, Pyridium, isoxazolyl urea, benzothiazole urea [16]. The classification of pesticides and the active compound of each group is shown in Table 2. Pesticide toxicity is the capability of a pesticide to cause injury to an organism. Exposure to pesticides is hazardous to the behaviour and well-being of humans and animal life which are often linked to a wide range of diseases [17]. Pesticides are classified according to the pest they kill as presented on Figure 1. The classification is based on the physical and chemical characteristics they possess. Such information is beneficial for determining the application method, rate, and precautions that need to be considered during the application. Within each class, there are many subclasses to expose the chemical content and examples of such pesticides.

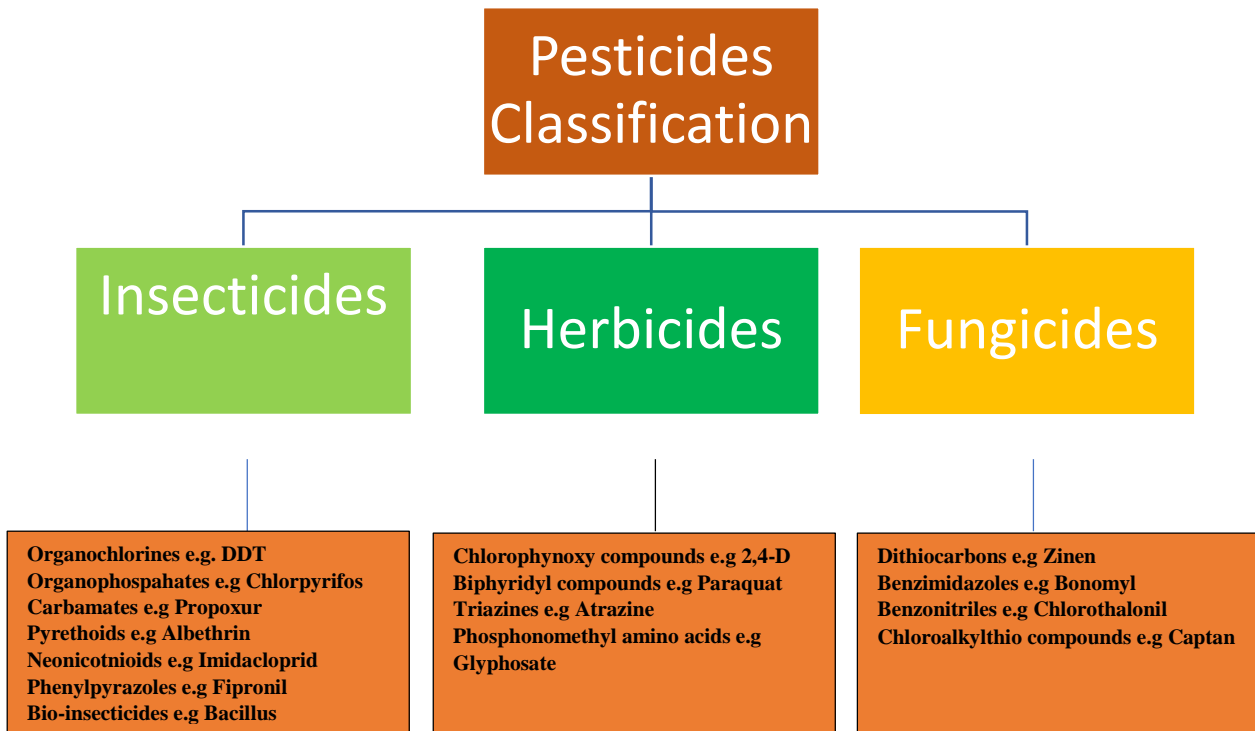


Figure 1. Classification of Pesticides Pesticide classification by pest they kill and the chemical composition Source: [17].

Pesticides and other forms of heavy metals used in the agricultural sector often find their way into the aquatic environment through runoff from the environment. They are however subject to airborne and water-borne hazards. The popularly known dichloro-diphenyl-trichloroethane (DDT) and lindane (-HCH) were widely used in the 1950s-1970s to control pests but due to its high environmental persistence and potential for long atmospheric transport the USEPA (1979) had to advise against the use of such of this organochloride.

The waterborne hazard is often derived from precipitation and then irrigation. These processes often the HM from surfaces of farmlands, into groundwater [18].

Pesticides are also organic micropollutants that have an ecological impact when introduced into agriculture to enhance and promote the production of food and produce. These Trace pesticides often get into water bodies and cause adverse effects to the life it inhabits and the environment.

The high rise in pesticide concentration and deposition in the environment causing pollution is often attributed to rapid urbanization, industrialization, economic growth, development of dynamic agricultural practices, and increased human and domestic activities [21]. Similarly,

[84] reported that bed sediment pollution can be dangerous for both ecological resources and human beings. Moreso, discharge from sludges and point source waste causing contamination should be regularly monitored and a cost-effective and environmentally friendly wastewater treatment plant should be installed to ensure the removal of PTEs before the discharge of effluents into the freshwater ecosystems. In agricultural protection against diseases and vectors and as well as protection of the natural environment, the intensive use of Organochloride Pesticides (OCPs) such as Hexachlorocyclohexane (HCH) and DDT has resulted in widespread environmental contamination, especially in the aquatic ecosystem. These pollutants accumulate in fish flesh, or tissues and organs through gills or the gastrointestinal tract during feeding and daily routine. In the aquatic environment, DDT once in fish can undergo biological transformation forming isomers such as DDD or Dichlorodiphenyldichloroethylene (DDE) [86]. Furthermore, it is reported that the frequent detection of these compounds in fish is because DDD oxidizes almost immediately in the oxygen-rich environment which fishes are mostly found [86].

### **Fertilizers**

Fertilizers are chemical substances with essential nutrients used by farmers and provided to crops to boost productivity. The essential nutrients include nitrogen, potassium, and phosphorus.

According to [14], Fertilizers can be grouped into

**Inorganic Fertilizers:** Inorganic fertilizers are chemical fertilizers that contain nutrient elements for the growth of crops made by chemical means. The inorganic fertilizers are of the following types: Nitrogen Fertilizers and Phosphorus Fertilizer,

**Organic Fertilizers:** Organic fertilizers are natural fertilizers obtained from plants and animals. It enriches the soil with carbonic compounds essential for plant growth. Organic fertilizers increase the organic matter content of the soil, promote the reproduction of microorganisms, and change the physical and chemical properties of the soil. It is considered to be one of the main nutrients for green food. Organic fertilizers can be obtained from the following products: Agricultural Waste, Livestock Manure, Industrial Waste, and Municipal Sludge Organic fertilizers, Crop residues, animal manures and slurries are the principal organic fertilizers. Although they have varying nutritional values, they are generally present on the farm and the nutrients and the organic carbon they contain are recycled.

**Compound fertilizers:** contain two or more nutrients and are also known as multi-nutrient fertilizers. A complex fertilizer refers to a compound fertilizer formed by combining ingredients to react chemically. Compound fertilizers can also be produced by blending two or more granular fertilizers of similar sizes. Such products retain the physical and chemical characteristics of individual compounds. They are made by mixing basic fertilizers derived from ammonia with salts containing phosphorus or potassium.

Streams, lakes and rivers surrounded by farmlands engaged in the use of Trace metal-enriched fertilizers have shown a possible and positive correlation to the rise in Trace metals from the



use of chemical, organic and water-soluble fertilizers for a long period. [24], reported that there is a tendency for high correlations of trace metals in source waters. Stating that the presence of one heavy metal could result in another, especially with the use of phosphate fertilizers. Furthermore, it is reported that source water from along farms from the application of manure, chemical fertilizer, organic fertilizer, compound fertilizer, and water-soluble fertilizer reveal the availability and accumulation of Trace metals to be significantly influenced by AP, TN, and IN, which are associated with fertilizer application thus posing a health risk to biodiversity in habitat [22,23,24]. A report by [83], revealed that in the major rivers of Pakistan (rivers of Sutlej, Ravi, Jhelum, Kabul and Jhelum), indices of Sediment pollution showed high levels of Hg and Ni concentrations which exceeded the guideline standards of river authorities in the world. The contamination factor (CF) and contamination degree (CD) indices for Hg, Ni, and Pb showed a moderate to high ( $CF \geq 6$  and  $CD \geq 24$ ) contamination level in all the selected rivers. High values of the geo-accumulation index (I) were also high ( $I_{geo} \geq 5$ ) for Hg and Pb as well as for Ni, Similarly, the enrichment factor (EF) values also revealed high values of ( $5 \leq EF \leq 10$ ) for Hg, Pb, and Ni.

### **Industrial sector**

#### **Geo-mining (quarry, blasting, crude oil mining)**

The introduction of Trace metal into water bodies can be through natural occurrences such as volcanic eruption, landslide and anthropogenic activities like all forms of mining, crude oil spills, pipeline vandalism, illegal bunkering of crude oil, and HM from untreated effluents. Heavy metals from such polluted sites are introduced directly through surface runoff into water bodies or indirectly through non-point source contaminants washed into water bodies [25]. In China, trace metals (As, Mn, Cr, Ni, Cu, Cd, Pb, and Zn) in water from mining sites and industrial locations were evaluated against their concentrations with the guidelines for drinking water versus surface water established by the China Environment Protect Agency (EPA) in 2002 and 2006. It was reported that the level of trace metals over time had increased significantly [24]. In Iludun-Ore and Environs in South-West Nigeria, the mining activities of tantalum niobium concentrates showed a high level of Pb, Fe, Cr, Sr, Mn and Ni [26,27], reported the capacity of characteristic sulphates ( $313.0 \pm 15.9 \text{ mg} \cdot \text{L}^{-1}$ ), carbonate ( $253.0 \pm 22.49 \text{ mg} \cdot \text{L}^{-1}$ ), and nitrate ( $86.6 \pm 41.0 \text{ mg} \cdot \text{L}^{-1}$ ), having extreme tendencies to enrich receiving environments with extremely high pollution load index ( $3.110 \pm 942$ ) for toxic metals/metalloid were observed in drains from Onyeama coal mine in Nigeria. The drains contained extreme levels of toxic metals/metalloid contamination and consequent astronomically high ecological risks in the order: Of lead > Cadmium > Arsenic > Nickel > Cobalt > Iron > Chromium.

In Jos, Nigeria, high levels of HM associated with mineral ores were found in soils and underground water from Tin mines. The eight HM (CR, Cu, ZN, PB, Co, As, Cd, and Ni) had concentrations above the Nigerian referred levels [28].

#### **Domestic waste (wastewater).**

Processed water from cosmetic industries, detergent industries, and textile industries often contains high levels of HM. The release of such waste into surrounding water bodies can lead to the destabilization of ecological stability organisms.

The presence and load of heavy metals are reported to be most in the gills, and liver and least in the flesh. In the common carp *Cyprinus carpio*, it was observed that Cd and Pb were most deposited at such organs respectively which is an indication of bioaccumulation [29].

#### Effects of trace metal in fish and man

Figure 2- Figure 4 show examples of damage made to fish gills, skin and liver of fish from various heavy metals.

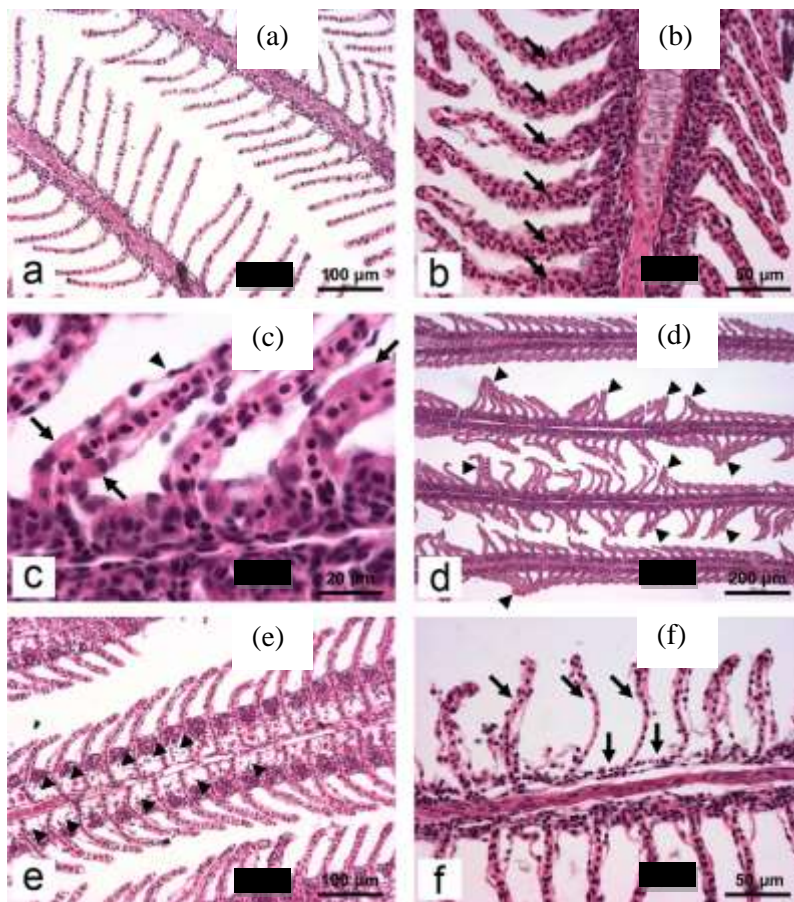


Figure 2. Micrographs of some of histopathological alterations found in the gills of common carp in the present study: a) normal tissue structure (H/E x200); b) note the extensive hyperemia on secondary lamellae (arrows; H/E x400); c) hypertrophy of squamous epithelial cells (arrows); compare thickness of these cells to non-pathological cell (arrowhead). Furthermore, note the size of the nuclei in both type of cells (H/E x1000); d) disturbed architecture of secondary lamellae: curling and fusion (arrowheads; H/E x100); e) oedema of primary filament (arrowheads; H/E x200); f) total rupture of epithelium leading to necrosis (arrows; H/E x400). [30].



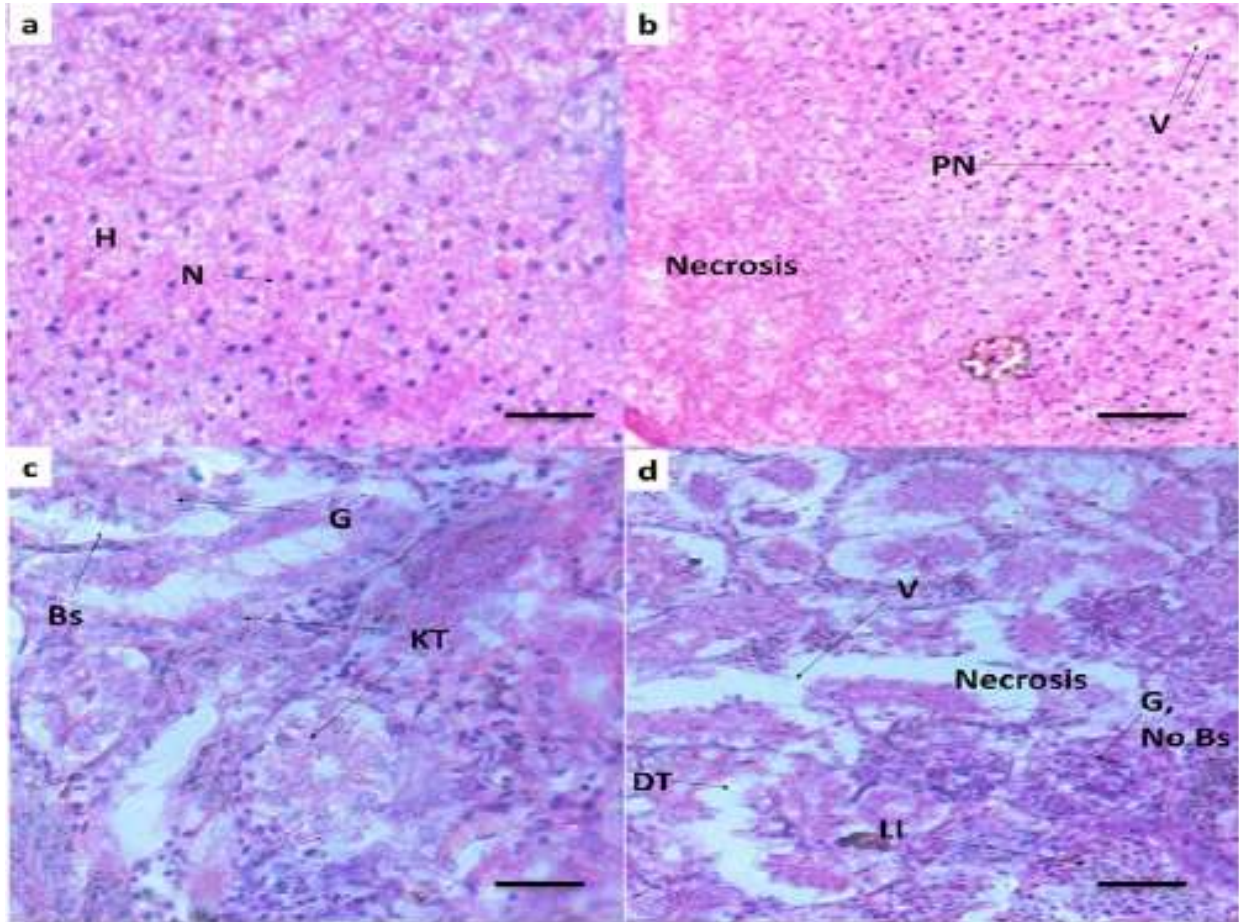


Figure 3. Liver of fish damages from trace metals. Bar scale = 40 µm, magnification 100×

Source: [31].

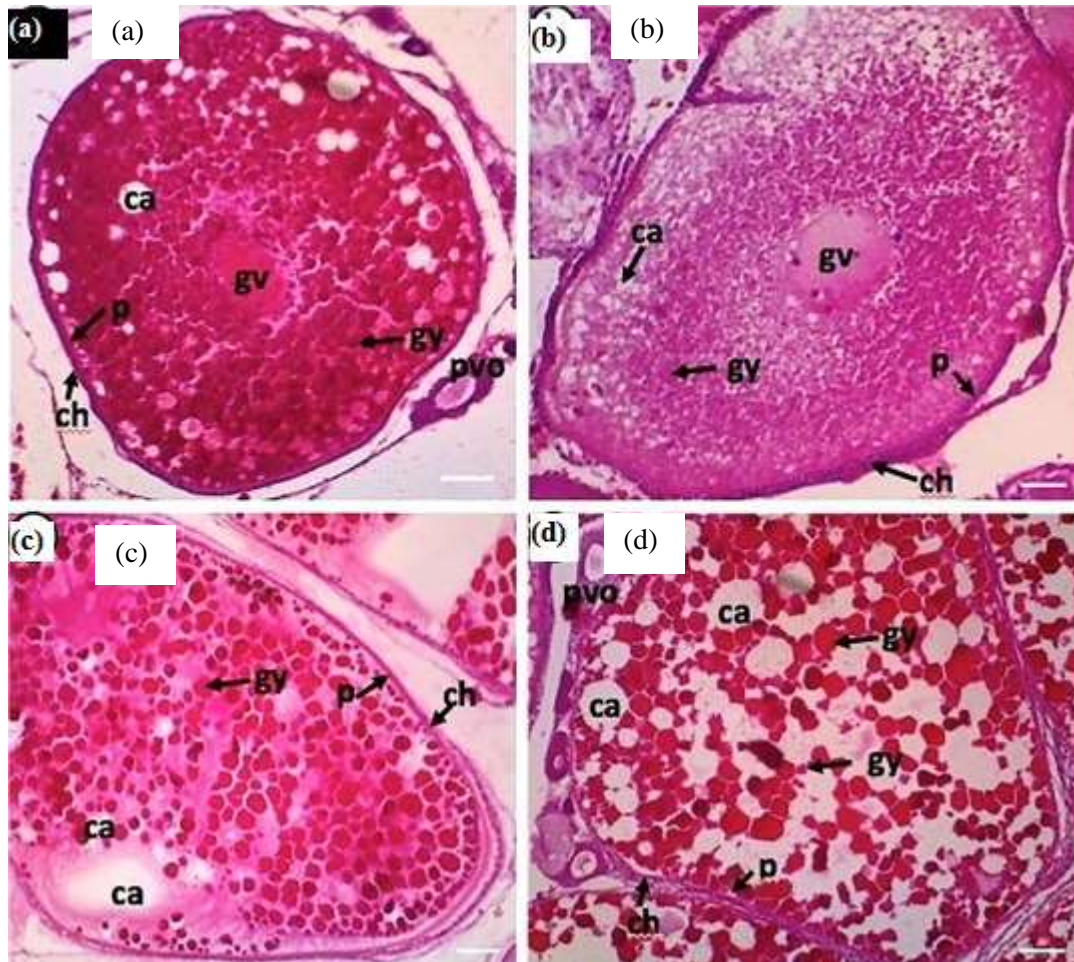


Figure 4. Damaged reproductive system of fish from trace metals.

Histopathological change of the Nile tilapia gonad (*Oreochromis niloticus*) due to the POME exposure: (a) treatment control, (b) treatment A, (c) treatment B, (d) treatment C. Germinal vesicle, gv; yolk granule, gy; cortical alveoli, ca; chorion, ch; previtelin, p; previtellogenic, pvo. Bar scale = 40  $\mu$ m, magnification 100 $\times$

Source: [32].

### Chromium (cr) in fish

Chromium is reported to have lesser accumulation on fish muscles compared to fish gills. Chromium shows poisonous effects in the blood such as anaemia, eosinophilia and lymphocytosis, and branchial and renal lesions. The EPA recommend that levels from 50 to 100  $\mu$ g Cr $\cdot$  L $^{-1}$  can be permissible for the management of aquatic life and for safeguarding human health [29].

### **Chromium in man**

Workers in the textile and steel industries are often affected by Cr (IV) which is harmful to human health. Other health issues are seen in tobacco smokers who are often exposed to high doses of it. Leather products from chromium are likely to cause allergies on the skin in the form of rashes, the nose is easily irritated and in extreme cases, the nose bleeds. In addition, the immune system is lowered, diseases of the skin, Irritation of the gastrointestinal mucosa, Nephritis, Lung cancer, liver and kidney damage, Necrosis, and death in men [33].

### **Mercury (Hg) in fish**

Mercury is taken up during ingestion and passed on to the liver where its action is distributed. Mercury is one of the TM most toxic to fish. In the liver, it binds, stores, and redistributes the mercury through surface circulation into various tissues and organs such as the gill tissues, liver and mostly the kidney. In these tissues and organs, the TM has often accumulated over time hence bioaccumulation.

The toxicity of Mercury is accompanied by convulsions and ataxia, detachment of gills, the fusion of secondary gill filaments, inflammation and deterioration of the liver and blood vessels [34]. Low levels of Hg in the reproductive system in Zebra fish, *Gynotus carapo* affect the production and viability of the ovaries, eggs, sperms and survival of fry [35,36].

### **Mercury (Hg) in man**

Low concentrations of mercury even when trapped in vapours can lead to nervous disorders leading to total change of behaviour in men such as tremors, emotional instability, insomnia, memory loss, ulcers and cancers in the thyroid and kidneys. Mercury is poisonous causing mutagenic effects, disturbs cholesterol levels and high exposure can lead to death (greenfacts.org).

### **Lead (Pb) in fish**

Pb is a hazardous substance commonly characterized as a persistent Trace metal. It is a substance that occurs naturally in the environment however, its deposition is accumulated by increased activities of man such as the mining of base metals, manufacturing of all sorts of batteries, lead-based paints and lead fuels [37]. Lead finds its way into water from run-offs and discharge from industries, from the dissolution of old lead plumbing, and lead-containing pesticides, through precipitation, the fallout of lead dust, street runoff, and municipal wastewater. Pb can become toxic to fish when it is accumulated to a substantially high level [38]. Pb as a potent environmental pollutant affects the trophic levels in a food chain. Pb from system runoffs, industrial and sewage waste and are taken up by fish through ingestion and inhalation from the aquatic medium. High doses result in metabolic poisoning, irritability, anaemia as well as behavioural changes [39].

### **Lead (Pb) in man**

Man can be affected by Pb through inhalation, Pb can also be taken up from food intake which is then accumulated in the muscles, bones, blood and fat. Again, damaging various organs and



tissues in the body. Lead is reported to affect Newborns and young children even at low levels [40].

Pb is known to cause reproductive disorders osteoporosis (brittle bone disease) heart disease, high blood pressure, especially in men, anaemia, psychological disorders and IQ [41].

### **Arsenic (As) in fish**

Arsenic is a substance used in the agricultural sector for the production of pesticides and defoliants. It is significantly used to reduce and kill aquatic weeds that disrupt fishing areas [42]. Just like other HM, Arsenic can be stored in large quantities in water and organisms especially aquatic organisms [43]. Arsenic toxicity causes histopathological changes and defects in internal organs such as gills, kidneys, liver bile duct proliferation and parenchymal hepatocytes (Figure 2). Apoptosis of the heart muscles, enlargement of intestinal mucosa and submucosa, and acute exposures can lead to death [44].

### **Arsenic (As) in man**

The ingestion of high levels of inorganic arsenic causes negative effects on the human system. Some of such effects include skin diseases and cancers, reproductive effects, diseases of the lungs, liver, kidney and bladder, non-insulin-dependent diabetes mellitus and visual impairment in children [45, 46].

### **Cadmium (Cd) in fish**

Increased industrial activities in the 20th, and 21st century has led to enormous production, consumption, and release of cadmium. Such cadmium is often produced for industrial uses such as the manufacturing of batteries, electroplating, plastic stabilizers, pigments and fertilizers, agricultural chemicals, and pesticides. Also, sewage sludge then into farmlands that often run off into groundwater and surface water might also contribute to the contamination of aquatic habitats causing damage to fish tissues and organs hence fishes through bioaccumulation. [47,48], have reported anatomical and structural deformations in the liver of *Cyprinus carpio*, *Carassius auratus* and *Corydoras paleatus*. It was stated that cadmium caused noticeable wounds, discolouration and hardening of the liver. In a study to show the storage level of lipids in fishes was carried out in different organs of two fishes, the overall comparison showed that the total percentage of lipids in all six organs was greater in *Hypophthalmichthys molitrix* than in *Catla catla*. Although the concentration of heavy metals was higher in *Catla catla* than in *Hypophthalmichthys molitrix*, a heavy metal deposition allows biomolecules such as carbohydrates, proteins, and lipids to decline via oxidative damage. In both fishes, the concentration of lead, iron, and nickel was found above the permissible range as defined by the WHO, while chromium, zinc, cadmium, and copper were found below the permissible level [90]. The concentration of these metals was found different in different body parts of both fishes as shown in Table 3. Which demonstrates the level of accumulation of heavy metals in different tissues among fish species. The deposition level of heavy metals also varies with the aquatic environment. Furthermore, the presence of subcutaneous tissues and their lipid content added their effect to the accumulation of heavy metals. A higher accumulation of metals and lower lipid profile was found for *Catla catla*. The

presence of heavy metals was linked with oxidative stress conditions causing a lowering of the nutritional index of fish via degrading biomolecules like lipids, proteins, and carbohydrates [90].

**Table 3: Total lipids % and age in different body parts of *Hypophthalmichthys molitrix*, *Catla catla*, and their comparison collected from the water of Tanda Dam.**

Organs	Fish species		Comparison		
	<i>Hypophthalmichthys molitrix</i> lipids (%)	<i>Catla catla</i> lipids (%)	Lipid % of <i>H. Molitrix</i>	Lipid % of <i>Catla catla</i>	P≤
Head	38.42	32.55	38.42	32.55	0.0525
Gills	23.47	22.08	23.47	22.08	0.0194
Abdomen	19.73	16.00	19.73	16.00	0.0662
Tail	16.51	14.73	16.51	14.73	0.0362
Fins	11.75	6.37	11.75	6.37	0.1837
Scales	3.05	1.58	3.05	1.58	0.1957
Pvalue	0.0118	0.0184	—	—	—

Source [90]

### Cadmium (Cd) in man

Cadmium is a deleterious Trace metal and a by-product of Zinc production. It has an instant destructive impact on humans. Respiratory tract diseases and kidney problems resulting from kidney failure are the commonest diseases gotten from inhalation of cadmium dust. Compounds containing cadmium are carcinogenic thus easily causing cancer, it also causes weakening and total damage to bones. A significant amount has to be ingested to cause immediate poisoning and damage to the liver and kidney [49]. In a study of the hazard quotient possibly generated by fishes accumulated with heavy metals, it was observed that a range from 0.01 for Cu to 0.80 for Hg in the investigated fish species. In all fish species, the hazard quotient (HQ) for Cd and Pb was higher than the HQ safety limit of 0.20 (HQ>0.20), which is an indication that Cd and Pb levels within individual fish species posed harmful health effects to consumers. Also, HQ values for As in *Clarias batrachus*, *Clarias gariepinus*, and *Hemichromis fasciatus* exceeded the 0.20 safety limit, indicating that the concentration level of arsenic in the fish species may harm the health of the consumers. *Chrysichthys nigrodigitatus*, *Clarias gariepinus*, and *Clarias batrachus* had HQ values above 0.20 for Hg, which could potentially harm consumers. It should be noted that the concentration of Cu in all fish species was lower than the HQ safety limit of 0.20, expressing no potential health effect. [87]



### **Aluminum (Al) in fish**

Aluminium in water makes the water acidic which is toxic to fish life. The major organ of a target is the gill where it mainly disrupts the lamellar epithelial cells and the gill epithelium. These aforementioned dysfunctions result in the death of cells and consequently death. [50], reported that physiological and histological alterations are frequently observed in different fish species exposed to Al in addition to an appreciable reduction concentration as of Al as low as 0.52 mg·L<sup>-1</sup>. Some of such alterations are mainly related to cardiovascular, respiratory, reproductive and structural gill damage as well as liver and kidney damage [51].

### **Aluminum (Al) in man**

Al is not easily detected in the human body in trace amounts consequently it is believed that aluminium is rapidly excreted within a short time of uptake from the body. Residual aluminium has been detected in the skeleton, brain and other tissues of the body [52].

### **Chromium (Cr) in fish**

Chromium will find its way into the environment from discharge released from pharmaceutical industries, textiles and dyeing industries, discharge from leather tanneries, metal fishing, electroplating, mining, printing and photography and ceramics [1]. Inadequate disposal and proper treatment of such waste and effluents may lead to the presence of Cr (IV) in the immediate surrounding and aquatic environment, where it can cause harm [53]. The physicochemical parameters of a given water body especially surface waters determine the stability of chromium. Fish gills are the easiest point of uptake of Cr thus leading to accumulation in the tissues mainly through the liver and kidney. The concentration found in fish and other aquatic organisms is often higher and at lethal do then leading to the heart which may seriously affect the catabolic, anabolic and physiological activities furthermore, may deter the optimal growth and behaviour of fish [54].

### **Chromium (Cr) in man**

Chromium is an essential nutrient metal necessary for the metabolism of carbohydrates [1]. Chromium in man causes mucosal irritation, phytotoxic corrosion, and irritation of the central nervous system which is followed by depression and in rare cases death [55].

### **Copper (Cu) in fish**

Copper (Cu) is an essential trace metal. It is a necessary element needed in living organisms for cellular respiration. It is a natural element that occurs in abundance and is widely used for many purposes [56]. Copper pollution comes from the persistent use of pesticides, fungicides, insecticides, nematocides, molluscicides, and algacides and the discharge of waste where copper is an active ingredient [57]. The concentration of copper in these chemical products is extremely high which is above the world's acceptable limits for life activities [58]. Copper is easily absorbed by the gills and readily stored in the fish liver. This accumulation is possible through diet uptake [58,59]. Common effects include gill and kidney alterations, and the production of large amounts of mucus on the body surface and gills. At high doses, lesions, discolouration and hardening of the liver is visible, as dysfunction of the reproductive organs,

reduced egg production per female, abnormalities in newly hatched fry, reduced survival of young, induced poor growth, decreased immune response, shortened life span [60,61,62].

### Copper (Cu) in man

High and lethal doses of Copper exposed to man can lead to oxidative damage in the brain which causes both Mense disease and Wilson disease. These diseases occur from the accumulation of Cu in the brain and eyes. This disease is fatal [62]. Other negative effects of Cu include abdominal disorders, damage to the kidney and possible death [61,62,63]. The results of the study conducted by [87] in Epe Lagoon, Lagos state, Nigeria revealed that the bioconcentration factor of water was greater than those of sediments. All the bioconcentration factors of water were greater than 1.00 except Cu in all samples, Mn in S3, S4 and S5, Fe in S1 – S5 and Pb in S1 – S8, S10. On the other hand, the BCF for sediment were relatively lower than the 1.00 recommended limits of WHO/FEPA except for iron in S7, lead in S9 and cadmium in S4. This indicates that the fishes undergo bioaccumulation of these metals from Epe Lagoon and hence the presence of metals in these fishes biochemically showed that fish is relatively dependent on the levels of metals available in an aquatic ecosystem. Table 4 shows International guidelines for heavy metals in fish, sediment and water.

Table 4: Hazard quotients (HQ) of heavy metals in selected fish species in the Densu River.

Fish species	Heavy Metal					
	As	Pb	Cu	Hg	Cd	HI
<i>Macrobrachium rosenbergii</i>	0.15	0.38	0.03	0.12	0.36	1.04
<i>Clarias batrachus</i>	0.49	0.43	0.03	0.80	0.55	0.29
<i>Clarias gariepinus</i>	0.68	0.58	0.04	0.80	0.76	2.85
<i>Chrysichthys nigrodigitatus</i>	0.08	0.03	0.04	0.22	0.31	0.95
<i>Hemichromis fasciatus</i>	0.23	0.33	0.01	0.09	0.27	0.92

Source: [88]

### Iron (Fe) in fish

Iron which is a naturally occurring element is a necessary component in industrial and mining companies as well as a source from which the resulting effluents are often discharged into aquatic environments [47]. Iron is most harmful and deadly at higher concentrations to aquatic life. Iron does not dissolve in water so living organisms cannot process and metabolize the amount ingested. The report has shown that iron causes flakes over gill tissues hence resulting in their respiratory disorders and possibly the total loss of the gills to necrosis (Figure 2). Other reports show a decrease in activities of the liver (Figure 3) and gonads, decreasing activity of the brain, muscles and heart [63].

### Iron (Fe) in man

Excess Fe in humans causes the malfunctioning of the general body metabolism. It induces stress in living organisms. Excess Fe is also related to inflammatory problems such as disorder

of the central nervous system, and neuronal degradation resulting in Parkinson's and Alzheimer's disease [64,65].

### **Nickel (Ni) in fish**

Nickel is a ubiquitous element obtained from natural resources and widely spread into the environment through anthropogenic activity. Reports on the adverse effect of lethal and high concentrations of Nickel are reported by [66], where fish species showed exploratory behaviour such as a decrease in appetite leading to significant growth retardation. Nickel exposure is said to induce some histological changes in the anatomy of *Oreochromis niloticus*. Structural changes include hyperplasia, hypertrophy, shortening of secondary lamellae and fusion of adjacent lamella, the significant rise in the level of blood glucose, liver and pancreatic disorders causing hypercholesterolaemia, hyper protein anaemia and hyper albumin anaemia (Figure 2, Figure 3, Figure 4) [67,68]

### Effects of nickel (Ni) in man

Extreme doses of Ni are reported to primarily cause contact dermatitis. If inhaled, it is said to be deposited and affect the lungs, heart, diaphragm, bones, brain and spinal cord. High concentrations can cause nasal fibrosis, and DNA damage [69,70].

### Effects of zinc (Zn) in fish

Zinc is an essential trace element occurring naturally in the environment. Zn is necessary for cellular synthesis in living organisms [71]. Zinc is deposited in the environment from zinc chlorides, ironwork, residues of paints and plumbing work. Deposits of zinc which make the aquatic environment toxic become lethal to the life of fish [72]. Just like other heavy metals Zn wastes easily affect the gills causing complications to the respiratory system. At high concentrations, it may be toxic to fish leading to a gradual decline in the immune system, reproductive capability and growth (figure 4) [73,89].

### Effects of zinc (Zn) in man

There are no known negative effects of the toxicity of Zn in the literature. However, one study has it that high doses and exposure to Zn in men may cause a lack of muscular coordination [74].

In Nigeria, most of our water bodies serve as reservoirs for drinking and domestic uses, making the distribution of Trace metals and pesticides in the aqueous phase, suspended particles and sediments unavoidable. This accumulation of pesticides in our water bodies is a major public health concern [75]. In the aquatic environment, organisms are exposed to pesticides through contact with the gills, skin, ingestion or inhalation into the gastrointestinal tract and muscles. Within the fish, the HM is either broken down, used up, released or stored. Trace metals are taken up by different fishes in different forms at different rates according to various factors. It could be due to environmental factors (water chemistry, salinity, temperature, and levels of contamination or biological) or biological factors (species, size, gender, sexual maturity, and food source) in addition as recently discovered by [85], indicating that hydrophobicity is one

of the key factors influencing the bioaccumulation potential of the heavy metal compounds. From polluted rivers which eventually are transported to humans [76,77].

Standard indices in human health risk assessment were used to estimate non-carcinogenic implications associated with consuming *Clarias batrachus*, *Clarias gariepinus*, *Hemichromis fasciatus*, *Chrysichthys nigrodigitatus*, and *Macrobrachium rosenbergii* from Densu River, the report revealed that heavy metal concentration showed a significant increase in the order of surface water < pelagic fish < benthic fishes < sediments. The Cadmium and Lead levels in all investigated fish tissues exceeded FAO/WHO recommended standards. Pb, Cd, and Hg mean concentration levels in the water exceeded the WHO threshold level of 0.01, 0.003, and 0.001mg/kg, respectively. The concentration level of all sediment samples was below the USEPA set limit for analyzed heavy metals. Furthermore, the correlation analysis revealed that *Hemichromis fasciatus* was identified as an applicable bioindicator for assessing heavy metal pollution because it correlated with water and sediment significantly. Moreso, the Principal component analysis ascribed heavy metal pollution in the Densu River to anthropogenic activities along the river. Although the interpretation of estimated daily intake computation showed that the content of individual heavy metals in the fish is not likely to endanger the health of the consumers, it was however recorded that the hazard index for *Clarias gariepinus*, *Clarias batracus*, and *Macrobrachium rosenbergii* exceeded one (HI>1), an indication of cancer risk to consumer [88]. Trace metals do affect living organisms through bioaccumulation. These Trace metals enter the food chain from the primary producers and affect the whole chain most especially fish [77]. Fishes are often the most vulnerable and are affected directly, particularly because the aquatic environment is their habitat and source of food constantly exposed to pesticides and Trace metals. Consequently, the toxic effect of these HM affects the fish by decreasing food sources, the food chain is disrupted, leading to a lowering aquatic habitat [77, 78,79].

The report has it that ability and capacity of trace metal to be deposited in fish depends on the concentration of metal and time of exposure, nature of the water, pH, hardness and alkalinity and dissolved oxygen, sex and age of fish, season and habitat [77]. Trace metals are taken up primarily from the environment through gills, food, and skin then are carried to organs and tissues as shown in table 5 [89,90].

**Table 5: Noncarcinogenic analysis of metals in fish samples.**

Fish species	Pb		Cd		As		Hg		Cr		Zn	
	EDI	THQ	EDI	THQ	EDI	THQ	EDI	THQ	EDI	THQ	EDI	THQ
<i>Mormyrus rume</i>	0.04	0.03	0.01	0.01	1.07	3.6	0.36	1.2	5.32	1.8	3.5	0.01
<i>Leptocypris niloticus</i>	0.38	0.25	0.01	0.01	0.55	1.8	0.39	1.3	11.5	3.8	4.18	0.01
<i>Oreochromis niloticus</i>	0.08	0.38	N/A	N/A	0.05	1.8	0.21	0.69	9.64	3.2	3.85	0.01
<i>Chrysichthys johnelsi</i>	0.03	0.19	0.01	0.01	0.77	2.6	0.56	1.9	11.8	3.9	4.36	0.01
<i>Clarias gariepinus</i>	0.05	0.30	0.01	0.01	0.36	1.2	0.38	1.2	5.75	1.9	3.85	0.01
<i>Parachanna obscura</i>	0.014	0.09	0.004	0.003	0.56	1.9	0.56	1.9	6.39	2.1	4.4	0.15
<i>Sarotherodon melanotheron</i>	N/A	N/A	0.004	0.004	0.39	1.3	0.73	2.5	6.35	2.1	3.01	0.01
<i>Ctenopoma gariepinus</i>	0.004	0.002	0.004	0.004	0.93	3.1	0.72	2.4	14.4	4.8	4.46	0.01
<i>Sarotherodon galilaeus</i>	0.007	0.005	N/A	N/A	0.917	3.0	0.721	2.4	20.8	6.9	4.46	0.01
<i>Ctenopoma kingsleyae</i>	0.007	0.005	N/A	N/A	0.906	3.0	0.899	3.0	18.7	6.2	3.605	0.01

N/A means not applicable; Target hazard quotient (THQ); Estimated Daily Intake (EDI)

Source: 89

Small fishes are affected more than larger ones. Again, freshwater fishes are more affected than saltwater fishes. Following a comparison in the magnitude of accumulation of trace metals between marine and freshwater fishes, [78], observed that freshwater fishes tend to accumulate trace metals 6 times more in their organ than marine fishes. The reason for such a difference is that freshwater tends to lose salts and gain water as against marine species. Furthermore, concentrations of Trace metals are elevated in the wet season in the environment and fish tissues than in the dry season ( $p < 0.05$ ) [4].

Researchers have suggested that carnivorous fish species which are often predatory and are at the highest trophic levels accumulate more Trace metals as against Omnivorous and Herbivorous fish because carnivorous fish, which mainly eat other organisms at the lower trophic levels such as fingerlings, shrimp, crustaceans and zooplankton, thus will consume more amount of metals in the body, unlike the non- predatory and carnivorous fishes with varying diets of insects, shrimps, small fish, crustacean, algae, plankton and detritus of [33,80].



Thus, the accumulation of HM in fish may have been due to the diversity of feeding habits and behaviour. The report of [86] revealed that pelagic fish had relatively higher Zn and Cu concentrations while demersal fish had higher Cr concentrations, the study proved that exposure due to fresh contaminants from riverine discharge is higher than that from benthic flux from historical contamination, a higher contaminant accumulation occurs in pelagic fish than in benthopelagic fish. However, this is thought to be the due to the type of discharge concerning the type of fish disposed of.

## CONCLUSION AND RECOMMENDATIONS

The ingestion, absorption and uptake of trace metals in fish are usually toxic and result in harmful damage to the fish and fish life. Since most of the metals taken up are non-biodegradable, such metals can bioaccumulate and bio-magnify. Over time, the accumulated metals affect the growth and development stages of fish from the production of viable eggs, hatchability laval, fingerlings and juvenile life stages. This is so because the early life stages are more sensitive than during maturing and adulthood. Fish is a delicate route for the transfer of toxic trace metals to the man from the water. The harmful effect of trace elements is numerous with varying degrees of destruction to human life and health. Since living organisms can generally not metabolize trace metals hence bioaccumulation and biomagnification, consequently it is of import that Trace metals should not be consumed above the national and international limits permissible by Law and Governing bodies such as UNESCO, WHO, UNDP and USEPA. Trace metals can be neurotoxic, carcinogenic teratogenic and mutagenic causing poisoning such of which are vomiting, convulsions, paralysis, ataxia, hemoglobinuria, gastrointestinal disorder, diarrhoea, stomatitis, tremor, depression and pneumonia.

It is therefore recommended that in Nigeria and as a global health concern, the assessment and treatment of all forms of waste from agricultural waste, sewage, and industrial effluents be carried out before their discharge into the environment, especially in local communities. Also, the enforcement of all laws and legislations at national, local and community levels regarding the protection of aquatic life and the environment be enforced and sanctions mitted against defaulters.

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**Highlights:**

The highlights of this manuscript include;

1. The effects of trace metals in the environment
2. The effect of trace metal on fish and man
3. The dangers of bioaccumulation of the trace metals in fish and man.

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