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International Journal of Current Research
Vol. 8, Issue, 09, pp.39266-39270, September, 2016

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

REVIEW ARTICLE

REVIEW OF COPPER AND ITS TOXICITY IN FISHES

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ARTICLE INFO

Article History:
Received 19th June, 2016
Received in revised form
23rd July, 2016
Accepted 15th August, 2016
Published online 30th September, 2016

Key words:

Copper, Cirrhinus mrigala, Review,
Bioassay, Physical and Chemical properties.

ABSTRACT

This study evaluates the toxicity of copper in aquatic organisms like fishes and the changes were observed in different parameters including the physico-chemical parameters. Copper cause harmful effects on metabolic, physiological, and biochemical systems of fishes and it causes long-term eco-toxicological effects. Copper contamination in the aquatic environment is a potential threat for aquatic organisms, when exposed to significant amount as consequences of industrial, agricultural and anthropological activities.

Citation: Dr. Y. Thangam, 2016. "Review of copper and its toxicity in fishes", *International Journal of Current Research*, 8, (09), 39266-39270.

INTRODUCTION

Aquatic pollution is greatly affecting the metabolism of fishes and its heavy mortality has been experienced. A major part of the world's food is being supplied from fish sources, so it is essential to secure the health of fishes. Aquatic ecosystems that run through agriculture areas have high probability of being contaminated by runoff and general water leaching by a variety of chemicals. Fish has encountered several serious aquatic pollution problems. Unlimited use of chemicals, pesticides, salts and fertilizers have affected the aquatic ecosystem adversely and also the immune system of the aquatic animal. Among the heavy metals, copper has been regarded as strongly toxic to fish and other aquatic animals. However, little is known about the effects of copper on stress modulation. Copper is a co-factor for a number of enzymes including cytochrome C oxidase and is thus essential for respiration in all eukaryote cells. The redox nature of copper makes the element a potent toxicant. Tight regulation of organ and cellular copper concentrations has therefore evolved to ensure sufficient copper for essential processes while at the same time preventing toxicity arising from copper excess (Sloman 2004). Aquatic organisms including fish accumulate metals many times higher than present in water or sediments, thus causing an adverse effect on the aquatic organisms. These metals concentrate at different contents in organs of fish body. Accumulation of trace metals in the benthic invertebrates and fish species and effluent of electroplating industry containing heavy metals, in an industry which exerts an impact on aquatic organisms (Kaur and Kaur 2006). Effect of different heavy metals on the aquatic organisms has been studied by many workers. Copper is an essential trace element that plays a vital role in the physiology of animals for foetal growth and early post–natal development, for hemoglobin synthesis, connective tissue maturation especially in the cardiovascular system and in bones for proper nerve function and bone development and inflammatory process. It is involved in different biochemical process of animal metabolism such as, enzyme – co enzyme catalytic reactions. It is associated with the function of a number of enzymes such as oxygenase including cytochrome C oxidase and copper- zinc super oxide dismutase and ion transport for instance with ceruloplasmin (ferroxidase1), a putative copper transport protein required for the incorporation of iron transferring in plasma. The inorganic ions play an important role in osmotic phenomena and in the regulation of cellular metabolism. These are required by animals to provide suitable medium for protoplasmic activity. Fresh water fishes are hyper osmotic to their medium and they gain water osmotically and tend to lose solutes by diffusion. Aquatic bodies are the traditional recipients of industrial wastes containing heavy metals, which when released in higher concentrations cause deleterious effects on organisms. Copper is considered to be a necessary trace element for plants and

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animals. It is a unit of many metalloenzymes and respiratory pigments. Copper also attends to, as the oxygen connecting site in haemocyanin and the respiratory blood pigment. However, copper becomes toxic to aquatic biota when biological necessities are exceeded. Many studies indicate that copper in the water is held in solution essentially by complexation with naturally happening organic ligands. In freshwater, organic ligands are more important in obligatory copper than inorganic ligands containing sulfur, phosphorus, chloride, nitrogen. Dissolved organic-copper include complexes with amino acids, carboxylic acids, humic acids and various copper compound. The closeness of copper for humic acids is greater than for fulvic acids. The shock of copper on the aquatic environment is complicate and depends on the physicochemical characteristics of water Alkalinity, hardness and pH forcefully influence copper speciation in water and, so, its bioavailability for absorption by fish. Copper speciation is directly affected by water pH and the free cupric ion concentration is higher in water with low pH, while copper hydroxide complexes prevails in water with high pH. Copper toxicity in aquatic animals is lower when chelating factors such as EDTA and NTA, humic acids and suspended solids are present in water and is known to be higher in soft water than in hard water (Roja sadat jalali Mottahari *et al*., 2013).

Fish are an important component of human nutrition, and those from contaminated sites present a potential risk to human health. Since fish occupy the top of the aquatic food chain, they are suitable bioindicators of metal contamination. Metals are well-known inducers of oxidative stress, and assessment of oxidative damage and antioxidant defenses in fish can reflect metal contamination of the aquatic environment. Metals, especially heavy metals, like copper are important contaminants of aquatic environments worldwide. Metal pollution has increased with the technological progress of human society. Industry, mining, advanced agriculture, household waste, and motor traffic is all among the activities considered to be major sources of metal pollution. Metals can accumulate in aquatic organisms, including fish, and persist in water and sediments (Luoma and Rainbow, 2008). Speciation of metals, their solubility and complexation, are important factors that influence the toxicity of metals in the aquatic environment. The amount of dissolved metal strongly depends on water pH. The interaction of metals can alter their toxic effects on aquatic organisms both positively and negatively. Different modes of exposure to metals also play a role in metal toxicity. Fish take up metals through the gills, digestive tract and body surface (Kamunde *et al.,* 2002). Heavy metals like copper are absorbed through gills and gastrointestinal track by fish organisms, free of the uptake way they are chiefly accumulated in metabolically active tissues such as liver and kidney. Gills are indirect contact with the outer environment therefore with the pollutants. Liver acts in the transformation of basic nutrients and in detoxification on storage of toxic materials. The interference in the gas exchange, nitrogenous waste excretion, acid-base and ionic stability due to the change in water pH cause stress in fish affecting its body physiology and growth. Large concentrations of $CuSO_4$ damage the gill epithelium, hematopoietic tissues, kidney, spleen and liver of fish (Figueiredo –Fernandes *et al*., 2007). Consequently, they alter the blood parameters (Carvalho and Fernandes, 2006) and osmoregulation (Singh *et al*., 2008). Immunosuppression can also be observed, due to the fact that monocytes and neutrophils are sensitive to heavy metals. Blood assessment constitutes an important tool to evaluate the fish health and may vary according to toxicants. Copper (Cu^+) toxicity is influenced by water alkalinity and hardness; hence, when used in water with low concentrations of $CaCO_3$, the ion Cu^{++} may cause physiological changes in fish. The cupric ion interferes in the linking of ionic regulatory proteins by obstructing their regulatory function. In fish, Cu^{++} is an essential trace metal for metabolic functions. However, it is potentially toxic when the internal available concentration exceeds the capacity of physiological detoxification processes (Figueiredo –Fernandes *et al*., 2007). Fish exposed to environmental pollutants exhibit a variety of physiological responses, including blood balance disturbances.

Review

Copper is an essential micronutrient for vertebrate animals especially fish. It has numerous functions in cellular biochemistry including vital roles in cellular respiration, and a cofactor for over 30 different enzymes. Copper compounds are used for prophylactic purposes to control fish diseases and parasites. They also used to control algae, kill slugs and snails in irrigation water systems and municipal water treatment systems. Copper is a heavy metal with density greater than 5g/cm3, thus it is toxic and poisonous in relatively high concentrations. It is non biodegradable but easily assimilated and bio-accumulated. Elevated levels of copper may become acutely or chronically toxic to aquatic lives. Chronic effects include reduced growth, shorter lifespan, reproductive problems, reduced fertility and behavioural changes. Copper deficiency leads to physiological disturbances, symptoms which include depression of growth, anaemia, bowing of legs, spontaneous fractures, ataxia of new born, cardiac and vascular disorders, depigmentation, decrease in some organs weight, depressed reproductive performance including egg production and tissue accumulation rapidly adsorbed in particulate materials (Shaw and Handy, 2006). Copper inhibits the excretion of ammonia through the gills; increases cortisol levels, stimulates the protein catabolism and increases levels of blood ammonia (Grossell *et al*., 2002). Copper undergoes complex speciation in natural waters; some species are bioavailable (free $Cu2^+$ and Cu^+ ions), while others are not. Only bioavailable forms of copper are considered to be toxic to exposed organisms. The bioavailability, biodistribution to various parts of the organism, and bioaccumulation of copper are dramatically influenced by water chemistry. Therefore, water pH, hardness, organic content, and salinity play important roles in copper-induced toxicity. Maintaining target concentration levels of copper can be challenging. Keeping copper concentrations high enough is difficult for many reasons. Water has numerous dissolved compounds (for example, bicarbonate ion (HCO3), which can readily "combine" with copper and remove copper from solution. Copper can also be taken up by living organisms, including bacteria, algae, and brine shrimp, and it can bind to substrates in the system (including activated carbon). Still other factors can cause the copper concentration to rise too high. Increases in salinity will decrease the binding (absorption) of copper to surfaces. In salt water at more neutral pH (e.g., pH of around 7), copper is surrounded by chloride molecules. Decreases in pH will release previously bound copper, and increase levels in solution, thereby increasing the risk of toxicity. Also, if some live foods, such as brine shrimp, are present during copper treatments, they may bioaccumulate enough copper to be toxic to fish that eat them.

Fish are one of the most widely distributed organisms in an aquatic environment and being susceptible to environmental contamination may reflect the extent of the biological effects of environmental pollution in water. Fish are particularly sensitive to environmental contamination of water and pollutants may significantly damage certain physiological, biochemical and enzymological processes when they enter the organ of fish. For fish, the vast majority of investigations have been used fresh water species on environmental models. In aquatic organisms gills represent a vital organ, since they play an important role in the transport of respiratory gases and regulate the osmotic and ionic balance. Toxic substances may cause damage to gill tissue, thereby reducing the oxygen consumption and disturbing the osmoregulatory function of aquatic organisms. Although in terrestrial vertebrates stressor have many disturbing effects on hydrominernal parameters, in primary aquatic animals such as fish, the impact of stressors on water and ion homeostasis is one of the most characteristic aspects of stress in fishes; this is mainly caused by the very intimate relationship between the body fluids in the gills and the ambient water (Wendelaar Bonga, 1997).

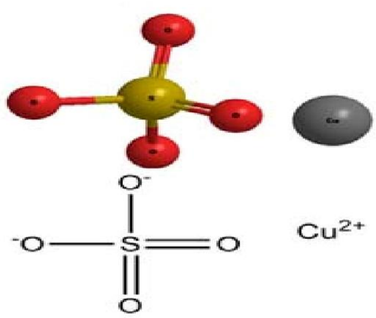
Investment casting was invented in 4500–4000 BC in Southeast Asia and carbon dating has established mining at Alderley Edge in Cheshire, UK at 2280 to 1890 BC (Timberlake and Prag 2005). Ötzi the Iceman, a male dated from 3300–3200 BC, was found with an axe with copper head 99.7% pure; high levels of arsenic in the hair suggest the involvement in copper smelting. Experience with copper has assisted the development of other metals; in particular, copper smelting led to the discovery of iron smelting. Production in the Old Copper Complex in Michigan and Wisconsin is dated between 6000 and 3000 BC (Emerson et *al*., 2009). Natural bronze, a type of copper made from ores rich in silicon, arsenic, and (rarely) tin, came into general use in the Balkans around 5500 BC. Previously the only tool made of copper had been the awl, used for punching holes in leather and gouging out peg-holes for wood joining. However, the introduction of a more robust form of copper led to the widespread use, and large-scale production of heavy metal tools, including axes, adzes, and axe-adzes.

MATERIALS AND METHODS

Bioassay

Of the two types of bioassay experiment viz., Continuous flow (Mount and Warner, 1965) and static method (APHA, 1998) the static bioassay method was chosen considering the limitation of laboratory facilities.

Chemical structure: Copper sulphate ($CuSo_4$)



Physical properties

Molecular formula : $Cuso_4$
Color : Blue crystals, white dehydrated
Odor : None
Molecular weight : 159.61
Melting point [^{0}c] : No data
Boiling point [^{0} c] : 3.60
Vapour pressure, 20^{0} c : No data
Specific Gravityofgas (20/4^{0}C) :2.286.

Chemical properties

Copper is the first element of Group IB of the periodic table and displays four oxidation states: Cu(O), Cu(I), Cu(II), and Cu(III). Along with silver and gold, it is classified as a noble metal and, like them, can be found in nature in the elemental form. Copper's unique chemical and physical properties have made it one of the most important metals. These properties include high thermal conductivity, high electrical conductivity, malleability, low corrosion, alloying ability, and pleasing appearance Copper is the chemical compound with the chemical formula Cu. This salt exists as a series of compounds that differ in their degree of hydration. The most commonly encountered salt, is bright blue. Other names for copper(II) sulfate are "blue vitriol" and "bluestone". Copper sulphate is blue, air sensitive. Harmful if swallowed. Causes digestive and respiratory tract irritation with possible burns. Causes eye and skin irritation and possible burns. Hygroscopic, mutagen, possible sensitizer. Target Organs: Blood, kidneys, liver. Copper toxicity to fish and its bioavailability in water vary with physicochemical properties of water, i.e., pH, alkalinity, suspended solids, organic compound content, and hardness. The concentration of free copper, cupric ion (II), increases with water acidity. Copper hydroxide predominates in water of pH 8.0 and higher (Tao *et al.,* 2001). Exposure to particulates or solution may cause conjunctivitis, ulceration, and corneal abnormalities. Cause itching eczema and when ingested causes severe gastrointestinal tract irritation with nausea, vomiting and possible burns. Ingestion of large amounts of copper salts may cause bloody stools and vomit, low blood pressure, jaundice and coma. Ingestion of copper compounds may produce systemic toxic effects to the kidney and liver and central nervous excitation followed by depression. Chronic: Prolonged or repeated eye contact may cause conjunctivitis. Causes liver and kidney damage, anemia and other blood cell abnormalities. Individuals with Wilson's disease are unable to metabolize copper. Laboratory experiments have resulted in mutagenic effects Chronic copper poisoning in man is recognized in the form of Wilson's disease.

DISCUSSION

Copper is an essential compound for aquatic organisms in small quantities. However, copper becomes toxic when biological requirements are exceeded. The effects of copper on aquatic organisms can be directly or indirectly lethal. Different species, and even organisms within the same species, can exhibit different sensitivities to elevated copper levels in the water column. Organisms have different mechanisms by which they cope with and process copper. Some organism bioaccumulate and store copper, whereas others actively regulate its levels. In general, copper is actively regulated in fish, decapod crustaceans, and algae are stored in bivalves, barnacles, and aquatic insects. Therefore, to properly evaluate the copper-related effects on aquatic life, one must understand the factors that affect the biological fate of copper and the mechanisms by which it acts to produce its toxicity. Wide range of contaminants are continuously introduced into the aquatic environment mostly associated with industrial, agricultural and domestic wastes run-off (Lima *et al*., 2008). Among these contaminants, heavy metals constitute one of the main dangerous groups, because they are toxic, persistent and not easily biodegradable. The species and concentrations of metals in water are determined by geochemical processes and large scale releases into the aquatic environment by human activities (anthropogenic activities). Rapid industrial developments as well as the use of metals in production processes have led to the increased discharges of heavy metals into the environment. The harmful effects of heavy metals as pollutants result from incomplete biological degradation. Therefore, these metals tend to accumulate in the aquatic environment. Since heavy metals are non-biodegradable, they can be bio-accumulated by fish, either directly from the surrounding water or by ingestion of food. In addition, when metals reach sufficiently high concentrations in body cells they can alter the physiological functioning of the fish. Copper has been known to humans for at least 6000 years. Its uses in alloys, tools, coins, jewelry, food and beverage containers, automobile brake pads, electrical wiring and electroplating reflect its malleability, ductility and electrical conductivity. The use of copper to kill algae, fungi and molluscs demonstrates that it is highly toxic to aquatic organisms. In fact, copper is one of the most toxic metals to aquatic organisms and ecosystems. This is one of the reasons that environmentally sensitive mining practices are so important. Fish are 10 to 100 times more sensitive to the toxic effects of copper than the mammals. This is an exception to the general principle that aquatic animals are more sensitive than aquatic plants to the toxic effects of metals (Okocha and Adedeji 2012). Copper occurs naturally as native copper and was known to some of the oldest civilizations on record. It has a history of use that is at least 10,000 years old, and estimates of its discovery place it at 9000 BC in the Middle East a copper pendant was found in northern Iraq that dates to 8700 BC. There is evidence that gold and meteoric iron (but not iron smelting) were the only metals used by humans before copper. The history of copper metallurgy is thought to have followed the following sequence: 1) cold working of native copper, 2) annealing, 3) smelting, and 4) the lost wax method. In southeastern Anatolia, all four of these metallurgical techniques appear more or less simultaneously at the beginning of the Neolethic 7500 BC. However, just as agriculture was independently invented in several parts of the world (including Pakistan, China, and the Americans) copper smelting was invented locally in several different places. It was probably discovered independently in China before 2800 BC, in Central America perhaps around 600 AD, and in West Africa about the 9th or 10th century AD (Cowen, 2009).

Conclusion

The Cu toxicity vary significantly among fish species due to other factors such as fish size, exposure dose time, species unique mechanisms for the metabolism of copper ion and physiological conditions of the individuals and also water physicochemical parameters. Thus, it is concluded that copper exposure indicate ionoregulatory or respiratory disturbances that imply an increase in energy consumption to restore homeostasis instead of other physiological functions and weight gain and growth. In conclusion, copper showed ionoregulatory interference, but also compensatory responses and allow fish to endure the changes that significantly affect the hematology, biochemical, hormone level, histopathology and ionoregulatory function in fishes.

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