# Effect and necessity of anthropogenic copper on fresh water aquaculture organisms: A review.

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# Abstract

The aim of the present review is to gather baseline information on the importance and toxic effect of anthropogenic copper on aquaculture organisms. The expansion of agricultural activities (pesticide), industry (especially lather industry), metal works (electrical manufacturing), urban inputs (effluent from publicly owned treatment works) and mining activities can cause increase of anthropogenic copper in natural environments. Copper is an essential nutrient at low concentrations, but it is toxic to aquaculture organisms at higher concentrations. In addition to acute effects such as mortality, chronic exposure to copper can lead to adverse effects on survival, growth, reproduction as well as alterations of brain function, enzyme activity, blood chemistry, and metabolism. Polluted water by anthropogenic copper seriously threatens human health due to bioaccumulation of copper in muscle and other tissues of aquaculture organism. What makes copper as serious toxicant is its attraction to biological tissue and its slow elimination from biological system. The toxicity of copper can be affected by dissolved organic matter (DOM), alkalinity level, water pH, age and size of fish, presence of live feed, acclimatization time.

Keywords: Copper, Anthropogenic, Heavy metal, Ion regulation.

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# Introduction

The discharge of industrial effluents, raw sewage wastes and other waste pollute most of the environments and affect survival and physiological activities of aquaculture organisms. Heavy metals in particular can affect aquatic biota and pose a risk to fish consumers. Metals come to the aquatic environment through human action like agricultural activities (pesticide and herbicides), urbanization and industrialization [1]. From time to time the expansion of industrial and urban imputes cause for the increase level of heavy metals in the environment [2,3]. Essential metals (e.g. copper (Cu), zinc (Zn), chromium (Cr), nickel (Ni), cobalt (Co), molybdenum (Mo) and iron (Fe)) have a known biological role, and toxicity occurs either at metabolic deficiencies or at high concentrations [4]. They believed to accumulate in the tissues of aquatic animals and become toxic when concentrations reach certain toxicity thresholds, values which vary considerably among metals, metal species, taxonomic species and organism life stages. Fish absorb metals mainly through the gills and the digestive track, and to a lesser extent, through the skin.

Heavy metals and organic compounds can be accumulated in aquatic biota [5]. Bioaccumulation is the net build-up of substances from water in an aquatic organism as a result of enhanced uptake and slow elimination of such substance [6]. Bioaccumulation measurements of heavy metals are very important because of their deleterious effect on the aquatic ecosystems [1]. The characteristics of some heavy metals are the strong attraction to the biological tissue and their slow elimination from biological system [7]. Since fish can occupy different tropic level they found to be good indicator of heavy metal contamination levels in aquatic systems [8]. Similar study by Azmat et al., also confirms fishes as one of the most significant indicators in fresh water systems for the estimation of metal pollution [9]. The toxicity level of heavy metals depend on the detoxification rate of metals, the habitat of the fish and concentration level of elements in the food [10].

## Source of copper

Copper is commonly found in freshwater ecosystem as a result of both anthropogenic and natural sources. Anthropogenic sources of copper include mining activities, agriculture, metal and electrical manufacturing, sludge from publiclyowned treatment works and pesticide use [11,12]. The level of copper can be increased in the environment due to the activities such as smelting of copper, industrial emissions, sewage, municipal wastes and fertilizers [13]. On other hand atmospheric Cu originates primarily from human activities such as Cu production (e.g. mining) and combustion of fossil fuel (coal, gas), the rest is from natural sources. In culture systems, Cu levels might increase due to antifouling and algaecide agents [14] Aquatic habitats are susceptible to Cu pollution because they are the ultimate receptor of industrial and urban wastewater, storm water runoff, and atmospheric deposition. Large quantity of heavy metal come from industrials effluents used to irrigate agricultural land and municipal waste water [15] which penetrate and accumulated in the tissue of the fish organ like gill and intestine via water.

## Necessity of copper in aquaculture organisms

Copper is important for growth and metabolism of all living organisms, including fish [16]. Copper ions are also required for the cellular processes such as respiration, neural transmission, tissue maturation, defense against oxidative stress and iron metabolism. In order to accomplish these important cellular processes sufficient intracellular copper ion level must be maintained. Copper is essential micronutrient for vertebrate animal especially fish, and cofactor for different enzymes (e.g. Cytochrome c oxidase, lysyl oxidase, dopamine-b-hydroxylase [17]. In addition to this, copper used in aquaculture organism tissue for ion transport with ceruloplasmin [18]. Ceruloplasmin is copper caring proteins produced in the liver and helps in transporting copper in fish blood. Many literatures reported copper has been used for many years to control algae and fish parasites in fresh water and marine water bodies. Copper sulfate is widely used in aquaculture in the concentration from 0.7 mg/L to 1 mg/L as a therapeutic agent to control algae and some pathogens in water [19]. Copper also used in small quantities for biological processes in aquatic plants.

#### Effect of copper on aquaculture organisms

Copper is an abundant element which occurs as a natural mineral with a widespread use. It is also an essential micronutrient for living organisms on account of being a key constituent of metabolic enzymes [4,20]. However it can be toxic to intracellular mechanisms at concentrations which exceed normal levels [21]. Too much of copper in the environment (e.g. from industries and agricultural activities) have negative effect on the health of fish. Similar study on copper found that Cu<sup>2+</sup> is more toxic than other toxic form of copper followed by CuOH and Cu (OH)2 [22]. Copper is also toxic to the nitrifying bacteria in the biofilter in recirculating aquaculture system (RAS). Bio filtration is a pollution control technique using a bioreactor containing living material to capture and biologically degrade pollutants [23]. At 0.3 mg/L Cu<sup>2+</sup>, copper sulfate inhibits ammonia and nitrite oxidation. Therefore, it increases ammonia and nitrite level in the system. Vutukuru et al, reported that presently, the increase of copper in aquaculture is interfering with the physiological function of fish [24]. However, different aquaculture organisms have diverse response to anthropogenic copper exposure (Table 1). Fish can accumulate copper via diet or ambient exposure. A fluctuation of the dietary copper load can lead to altered fish physiology with protein malfunctions [25]. Additionally, it is well documented in a variety of fish species, that excess waterborne copper exposure, will have deleterious effects on the gills, gut and sensory systems. Moreover, there are reproductive impairments, reduced growth and behavioral changes effects [26-35].

Table 1. Effect of copper in some selected aquaculture organisms.

Gill is an important site for the entry of copper [36]. Continuous accumulation of copper in the fish gills is due to the presence of positively charged copper ions that interact with the negatively charged gill. Similar study found that metal cautions, including Cu and Cd, bind to negative sites on fish gills [37], and metal toxicity to fish is determined by free metal ions that are bio available chemical species [38]. However, according to Schjolden et al., the copper challenge of approximately 300 µg Cu<sup>2+</sup>/l was not acutely toxic (96 h LC50) to crucian carp (Carassius carassius) [39]. Reduction in respiratory surface may lead to respiratory disturbance in teleost fish. Result of different article indicated that, the level of copper in lake and river range from 0.2  $\mu$ g/L to 30  $\mu$ g/L, but in contaminated water, the concentrations can rise to greater than 100 µg/L. In addition to this many publication agreed on high accumulation of copper in the body of fish leads to behavioral changes like shoaling nature, swimming with their belies upwards, loss of equilibrium and irregular movement.

#### Effects of copper on ion-regulation

The exposure of aquaculture organism to copper can damage a number of organs and systems like gills, liver, kidney, immune system, and nervous system. Among this organs gills seem to be the most affected organ during acute toxicity, and become thickened and lose ability to regulate body fluid ion concentrations. Other study shows, ion-regulation can be impair when copper exposed to crucian carp (Carassius carassius) and also they found that plasma sodium and chloride decreased during the exposure, while muscle tissue water content increased [39]. Eisler also found that ion regulatory dysfunction is commonly seen when fish exposed to copper [40]. Copper also interrupt the function of lateral line and reduce the growth of organism. Many studies agreed that reduction of Na<sup>+</sup> uptake is the first observed effects of copper exposure to the fresh water fish. Other study by Lauren and McDonald found that low concentrations of waterborne Cu can affect ion regulation by reducing Na<sup>+</sup> influx at the gills while higher Cu concentrations affect gill permeability causing increased ion efflux, probably due to displacement of

Aquaculture organism	Concentration of Cu (µg/I)	Effects	Citation
Coho Salmon	5-20µg/l	Reduction in olfactory response	McIntyre et al.,2008 [27]
		Reduction in appetite and food intake	McIntyre et al.,2008
		Reduce growth of salmon	McIntyre et al.,2008
		Reduce ability to detect predator	McIntyre et al.,2008
	5µg/l	Decrease downstream migration	Lorz andMcphase,1977 [28]
	20µg/l	Reduce swimming speed	Sandahl et al.,2007 [29]
		Reduce detectability of odors	Sandahl et al.,2006 [29]
Sea Scallops	10-20µg/l	Reduce sperm and egg production	Frances, 2009 [30]
	1.4µg/l	Produce physiological stress response	Taub,2004 [31]
		Increase blood level of the stress hormone cortisol	Taub,2004 [31]
Rainbow Trout	22µg/l	Loss of homing ability	Marr et al.,1999 [32]
	3.9µg/l	Increase diseases susceptibility	
	10µg/l	Impaired swimming ability	Atchison et al.,1987
Fathead Minnow	N/A	Reduce egg and sperm production	Taub,2004 [31]
		Reduce survivability	Taub,2004 [31]
		Increase abnormality	Taub,2004 [31]
Common carp	5.2µg/l	Gill damage	Sinha et al.,2016 [14]
	1.9µg/l	Gill damage	Baker et al., 1983 [3]
Chinook juvenile	2µg/l	Loss of avoidance ability	Hansen et al.,1999 [32]
Shore crab	0.5µg/l	Reduce heamolyph acidocis	Boitel and Truchot, 1989 [34]
Zebra fish	20µg/l	Damage to mechano sensory cells	Linbo et al.,2006 [35]

Ca<sup>2+</sup> from intercellular tight junctions [41].

According to Li et al., report reduction in Na<sup>+</sup> uptake was caused by inhibition of Na<sup>+</sup>/K<sup>+</sup>-ATPase at the Mg<sup>2+</sup> binding site and also due to additional effect of competitive nature between copper and sodium at the apical side [42] as copper may be passes through Cu-specific channel or leaks through sodium channel [17,43]. Schjolden et al., found that crucian carp (Carassius carassius) did not lose ions at the same rate as other fish species exposed to Cu<sup>2+</sup>. They also reported that it takes 4 times as long for crucian carp (Carassius carassius) to lose 20% of its plasma ions compared to rainbow trout(Oncorhynchus my kiss). De Boeck et al., found similar trend in ion loss occurs in gibel carp (Carassius gibelio) when exposed to sub lethal levels of copper [44,45]. According to Schjolden et al., the consequence of reduced plasma ion concentration in copper exposed crucian carp was a net movement of water from plasma to tissues [30]. Waiwood argue that increased heamatocrit in copper exposed rainbow trout was caused by movement of water from blood plasma to muscle tissue. According to Taylor et al., report rainbow trout and yellow perch (Perca flavescens) died from copper exposure (approximately 10 µg/l and 50 g/l respectively) within 96 h at the point when they had lost 60% of their whole body sodium [46,47]. In fresh water fish, copper is known to cause osmotic imbalance by reduction of brachial Na<sup>+</sup> uptake due to inhibiting the basso lateral Na<sup>+</sup>/K<sup>+</sup>-ATPase [48,49]. Reduction of brachial Na<sup>+</sup> uptake also decreases the uptake of Cl- which aggravates the ion regulatory disturbance, and NH, excretion is inhibited [50].

#### Bioaccumulation of copper in aquaculture organism tissue

Contaminants in the sediment are taken up by benthos and primary producer (periphyton, algae) in a process called bioaccumulation. When larger animals feed on contaminated benthos or primary producers the toxins are taken into their bodies, moving up the food chain with increasing concentrations in a process known as bio magnification [50]. This condition is true in mollusks (bivalve), herbivorous gastropods, barnacles and carnivorous gastropods organisms. Liver, gill and intestine have relatively higher potential for metal accumulation than muscle [51,52]. For instance, it was found that the higher accumulation ratios of metals in the liver could be due to the greater tendency of the elements to react with the oxygen carboxylate, the amino group and the nitrogen [53]. In liver, copper is attached to ceruloplasmin and also metallothioneins (MT) play important role in binding this metal in vertebrates. According to De Boeck et al., reported, metallothioneins (MT) are protective proteins that can sensitize as a result of metal exposure at the cellular level [54]. High accumulation of copper in the common carp (Cyprinus carpio) showed in the liver [55]. Gill copper concentrations decreased as hepatic copper concentration increased, in juvenile common carp. As study by McDonald and Wood indicated copper toxicity in fish shows a typical 'shock phase 'with extensive damage in the first hours or days of exposure and repair thereafter [56].

#### Factor affecting mechanism of copper toxicity

Environmental parameters such as water quality (temperature, pH, oxygen concentration, hardness, salinity, alkalinity, dissolved organic carbon, copper species concentration), interaction of copper with other elements, organisms: size, age and species affect copper toxicity to fish [13,57,58]. As studied by Playle et al., dissolved organic matter (DOM)

prevent adsorption of metals to the gills [48], by reducing the concentration of available free metal ions or by reducing the number of available binding sites, will reduce metal toxicity. Daly et al., also reported that, dissolved organic matter reduces the toxicity of Cu to fish by decreasing the number of free Cu ions through binding with dissolved organic matter (DOM) that lead to reduce the available Cu to interact at the gills [59]. The alkalinity and total hardness had effects on acute toxicity of copper to juvenile channel cat fish (Ictalurus punctatus). Study on rainbow trout (Oncorhynchus my kiss) reported that hardness is more important factor than alkalinity in protecting fish from copper toxicity. Different author reported that the effects of hardness are primarily function of calcium than magnesium. Example, Erickson et al., found that adding calcium chloride increase LC50 of copper by factor of 3.26 while magnesium chloride increase LC50 of copper only by factor of 1.09 when copper exposed to fathead minnow (Pimephales promelas) [50]. Cu is acutely toxic (lethal) to freshwater fish in soft water at low concentrations ranging from 10-20 ppb (NAS, 1977). Alkalinity, hardness, pH and dissolved organic matter are important parameter for predicting Cu bioavailability [22]. Dissolved organic matter (DOM) can be also one of the factors to mitigate toxic effect of copper in aquatic environments. Other study by Erickson et al. reported that at low pH the fish gill produce more mucus that bind to copper and slowdown copper uptake and stop the onset of toxicity. Bioavailability of copper can be measured by different tools like biotic ligand models. Biotic ligand model (BLM) is the model used to detect bioavailability of metals accumulated on the tissue of organisms.

## Conclusions

Copper is important micronutrients carries out vital function in animals (growth, reproduction and in osmo regulation) and at elevated levels it lead to physiological disturbance (suppresses immune system function, and can affect the lateral line of fish) to aquaculture organisms. Toxicity of anthropogenic Cu to aquatic organisms depends on its "bioavailability" or its potential to transfer from water or food to a receptor (gills, olfactory neurons) on an organism where toxic effects can occur. Copper can damage a number of organs and systems, including the gills, liver, kidney, immune system, and nervous system. Liver, gill and intestine have relatively higher potential for metal accumulation than muscle.

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