

EFFECTS OF COPPER ON AQUATIC ECOSYSTEMS - A REVIEW

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Abstracts: Impact of metal pollution has become alarming with the increasing industrialization. Copper is the most extensively used metal among other heavy metals. Copper and its alloys are being used almost in every industrial activity and also in our daily life. Copper as a micro-nutrient is essential for all living organisms at lower concentration for their optimal growth and development. But, copper in excess amount than required becomes toxic and the impact is more severe to the aquatic environment. In comparison to freshwater fishes and invertebrate, aquatic plants are equally or less sensitive to copper. Surface water systems should be managed and protected from pollution for the protection of fishes, invertebrates and to ensure aquatic plant survivability. Metal uptake rates will vary according to the organisms and the metal forms in the aquatic systems. The mechanisms of copper toxicity and storage are diverse as they vary with organisms and mode of uptake. Slightly elevated copper level in natural waters may cause sublethal effects in aquatic organisms such as histological or morphological changes in tissues, suppression of growth and development, poor swimming performance, change in bio-chemistry, change in behavior and change in reproduction. This paper mainly concentrates on recent development in the study of toxic metal (copper) species in the aquatic environment and its availability to the aquatic organisms and plants.

Keywords: Copper; Heavy metals; Pollution; Accumulation; Aquatic ecosystem

Introduction

Initially native copper has been used by man since about 8000 B.C., but smelting and the production of bronze implements date from about 4000 BC (Tiller and Merry, 1981). Of the heavy metals including chromium, manganese and nickel copper is heavier (Fergusson, 1990) and belongs to the third transition metal series, exhibiting a wide variation in properties such as complexing capacity and oxidation states. It has a $3d^{10}s^1$ electron configuration and is commonly found in the Cu^{2+} state with a $3d^9$ configuration in the aquatic environment. The properties of copper result from the partially filled d subshell. Elements with partially filled 3d shells tend to form complex ions with anions such as CO_3 , SO_4 , OH , and humic acid (Parker, 1981). The ability of copper to form a variety of complex ions poses a problem in estimating bioavailability and copper speciation in aquatic environment. In terms of toxicity, the $3d^9$ configuration allows copper to bind to sulfhydryl residues on proteins either on the cell membrane surface or within the cell.

In aquatic environment, copper can exist in three broad categories: particulate, colloidal, and soluble. Speciation of copper in natural waters is determined by the physico-chemical, hydrodynamic characteristics and the biological state of the water. The speciation of copper is

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directly linked to the bioavailability and toxicity of copper. Copper is most toxic in the free ion form prevalent at $\text{pH} < 7$ (Kennish, 1992). Various processes in the aquatic environment act to bind copper to inorganic and organic ligands which precipitate out of solution. Copper may also bind to particulates which settle out of the water column. These processes act to sequester copper in the sediment in a bound form making it less available and therefore less toxic to marine and freshwater organisms. As well, the presence of various complexing agents in the water column such as bicarbonate, carbonate, and hydroxide ions have a marked effect on the toxicity of copper. Toxicity is largely a function of the water chemistry and sediment composition in the surface water system (Connel and Miller, 1984).

Copper in surface water systems can be from natural or anthropogenic sources. Currently anthropogenic inputs of copper exceed natural inputs. Excess copper levels in surface water may pose a health risk to human and to the environment. Many organisms are able to regulate the metal concentrations in their tissue. Fish and crustacean can excrete essential metals such as copper, zinc and iron that are present in excess. Research has shown that aquatic plants and bivalves are not able to successfully regulate metal uptake. Thus bivalves tend to suffer from metal accumulation in polluted environments. In estuarine system, bivalves often serve as biomonitor organisms in areas of suspected pollution (Kennish, 1992).

Phytoplankton and zooplankton often assimilate available metals quickly because of their high surface area to volume ratio. The ability of fish and invertebrate to absorb metals is largely dependent on the physical and chemical characteristics of the metals (Kennish, 1992). The biological effects of copper in aquatic environment are concerned with lethal concentrations for individual species. Impacts of trace metals on population dynamics, species abundance, diversity and community functions are not clear. But changes in habitat size and species ranges in areas where effluent of high metal concentration is discharged are well documented (Rand and Petrocelli, 1985). Therefore, this paper will explore the effects of copper on aquatic ecosystems through a literature review.

Sources of Copper as a Pollutant

The majority of copper deposits are found around the Pacific rim and the mountain belts in southeastern Europe and central Asia. Areas in Australia and Siberia also contain relatively large deposits of copper. Estimate of Cu which has been emitted globally into the atmosphere from natural sources ranges from 10 to 18×10^3 tons annually and provide a general reference for the assessment of pollution. Man-influenced sources cause greater local impact and are quite significant globally (56×10^3 tons/year). The largest sources are windblown dust materials from bush-fires, volcanoes and plants exudates also contribute (Nriagu, 1990).

Batey *et al.* (1972) reported that excess copper in soil arises as a consequence of industrial or agricultural activities. Copper smelting and refining industries, manufacturers of copper products and sewage disposal processes all contributed to the man-made input of copper to the biosphere. Similarly, the use of copper based agrochemicals over extended periods could lead to excessive accumulations of soil copper in localized areas. The aquatic environment received additional copper through erosion of copper enriched soil as well as surface runoff water during rain.

The anthropogenic deposition of copper compounds into natural environment has increased steadily since the dawn of civilization. Much of the Cu pollution associated with industrial/urban activities is released from point sources from which dispersal is strongly dependant on local meteorological and topographical factors in relation to stack height and aerosol size (Tiller and Merry, 1981). At present industrial discharges of copper into the environment exceed natural fluxes by about 300%.

The total flux of copper to the atmosphere is approximately 75,000 metric tons per year of which 5000-13,000 tons are deposited into the ocean. Atmospheric emissions are the main route of entry to the environment. Through processes of wet and dry deposition, atmospheric copper enters into the hydrological cycle either by deposition onto soil and subsequent erosion into water bodies or direct deposition into rivers, lakes and oceans (Nriagu, 1990).

Accumulation

The mechanisms of toxicity and the storage of trace metals are diverse as they vary with organism, mode of uptake and chemical type. These contributing factors are important because they directly affect toxicity to aquatic organisms. Concentrations of uncomplexed metal ions are closely correlated with the uptake of cadmium, copper and zinc in crustaceans and fish. This relationship does not hold true for complexed metal ions because they require a carrier molecule to enable them to move through cell membranes (Lockhart *et al.*, 1992).

The availability of copper varies with the organism types, the system and plants have certain characteristic to exclude or accumulate copper in their tissue (Adriano, 1986). Accumulation of trace metals also depends on the tissue or organ. Metal concentrations of selected tissues of brook trout exposed to sublethal lead and methyl mercury solutions demonstrate the variability in tissue distribution of metals that occurs when animals are exposed to toxicants of different polarities and lipid solubilities. Accumulation is further complicated because many aquatic organisms are able to excrete elevated trace metal concentrations under contaminated conditions (Gerhardt, 1995).

Water pH is an important factor for copper availability. Copper and its complexes are readily available to the aquatic organisms below the neutral pH range (Hossain, *et al.*, 1999). Acidic water pH favours copper ions to be released from water column and hence absorbed by sediment (Smith, 1990). Major portion of up-taken copper by the aquatic plants comes from this sediment deposits. Aquatic plants are the primary producer, so copper gets the opportunity to circulate in the aquatic food chain from primary producer to consumer and accumulated in the fat body. The theory of food chain enrichment, where the highest trophic level contains the highest concentration of the toxicant, is not found to be true in the case of most heavy metals. Sediments contain the highest concentrations of trace metals causing sediment-feeders to have the highest concentrations of the biota. This further complicates the issue of accumulation.

Copper in Aquatic Ecosystems

Copper in trace amount is required by all living organisms. However, when present at concentrations higher than those required, it may become highly toxic. The normal concentration of copper in the open oceans and in river water ranged from 1-3 ppb (Goldberg, 1963) and 0.003 mg/L (Mullins, 1977) respectively. Depending on the sources of copper, its level both in coastal and river water varies widely throughout the world and high copper concentration in coastal areas can often be attributed to input from municipal wastes, industrial waste water and direct discharge of farm wastes to the aquatic environment.

The concentrations of copper sometimes encountered in coastal water and approach the incipient lethal concentrations for some marine animals (Calabrese, *et al.*, 1973). Relatively little published information on the sublethal biological effects of copper on fresh water invertebrates, fish and plants, is available.

Effect of Copper on Aquatic Invertebrates

The free cupric ion has been shown to be a dissolved species of copper which determine its toxicity to aquatic organisms (Seenda and Lewis, 1978). Copper is highly toxic to most fresh and marine invertebrates. Some species can adopt with high levels of copper and sensitivity is inversely related to the age and size of the organisms. Among invertebrates molluscs and malacostracan Crustacea seem to be the most susceptible than Oligochaeta with Diptera. Trichoptera and some other insects seem to be most resistant. Absorption of copper for marine invertebrates is found to be influenced with the variation of salinity in water bodies. Lang *et al.* (1981) has recorded more than 160 ppb copper concentration in Barnacle larvae (*Balanus improvisa*) at 30 ppt salinity at 15°C temperature and 80 ppb concentration of copper at the 15 ppt salinity at the same temperature. The factors involved in the toxicity of heavy metal like copper is numerous and complicated and also depends on the form of metal in water. Factors influencing the physiology of an organism such as salinity and temperature also contribute to the toxicity of heavy metals.

Neff and Andenson (1976) reported that a copper concentration of 500 ppb was acutely toxic to both the megalops and juvenile crab stage of *Callinectes similis*. However, 500 ppb copper concentration in exposure group cause mortality during the molt. But 250 ppb copper concentration is not acutely toxic to the juveniles crabs. Copper concentration of 64 ppb inhibited the growth and development of the *Tigriopus japonicus* and crustacean species (D'Agostino and Finney, 1974).

Role of copper on the metabolism and growth of decapod crustaceans have been reported by many investigators (Boon, 1973; White and Rainbow, 1983). Ayyavoo (1995) observed that copper is directly obtained from environment through permeable surface of gill and gut by decapod crustaceans. Martine *et al.* (1977) observed the presence of copper in respiratory pigments of crustaceans.

It is known that copper is toxic even in lower concentration and cause, physical problems (Ayyavoo, 1995) and is more toxic to *Ascartia spinicauda* and *Tortanus forcipatus* followed by cadmium and zinc (Madhupratap and Achuthanhutty, 1981). The rich deposition of copper is mobilized to other organs during moulting and reproduction. The hepatopancreas of shore crabs is capable of removing copper from circulating blood. Antennal glands can concentrate and excrete unwanted heavy metals. Due to this mechanism many crustaceans are capable of using detoxification and excretory process to afford some degree of protection against heavy metal pollution (Ayyavoo, 1995). Life cycle of aquatic organisms can be influenced by toxicity. A great deal of data exists on the concentration of a metal in aquatic organisms but provides little information about its actions in the environment and its effect on organisms.

Effect of Copper on Fishery Resources

Copper is usually more toxic to freshwater fish than any other metals except mercury but it is an essential of many enzymes. Copper is less toxic to marine fish due to the high complexing capacity of salt water. Short-term copper deficiencies or excess may be regulated by a variety of organisms thus minimizing its potential toxic effect (Forstner and Wittmann, 1983). Chronic copper toxicity results in the deposition of copper in the liver, kidney and other organs. Accumulated copper in the liver of rainbow trout results in increase in the number of lysosomes increased, mitochondrial swelling, mitochondrial degeneration, interruptions in the plasma membrane and large number of necrotic cells. Copper may also cause problems within the cell and forms complex compound with various enzymes and proteins resulting in impairments of function or complete inactivation (Pelletier *et al.*, 1993). Acute toxicity of copper to different fish species is shown in the Table 1.

Table 1. Acute toxicity of copper to fish: selected samples from literature.

Species	Copper concentration (mg/l)
Brook trout (<i>Salvelinus fontinalis</i>)	0.1
Atlantic salmon (<i>Salmo salar</i>)	0.03
Rainbow trout (<i>Salmo gairdneri</i>)	0.9
Coho salmon (<i>Oncorhynchus kisutch</i>)	0.046
Goldfish (<i>Carassius auratus</i>)	0.46
Carp (<i>Cyprinus carpio</i>)	6.4
Fathead minnow (<i>Pimephales promelas</i>)	0.075
Rudd (<i>Scardinius erythrophthalmus</i>)	0.6
Stone loach (<i>Nemacheilus barbatulus</i>)	0.76
Pike (<i>Esox lucius</i>)	3.0
Perch (<i>Perca fluviatilis</i>)	0.3
Bluegill (<i>Lepomis macrochirus</i>)	10.2
Eel (<i>Anguilla anguilla</i>)	0.81

Source: Haslam, 1991.

It is difficult to assess ecological effect on communities when communities are not studied. Fish have home range and territories within which they usually move. However, they will go out side to get away from pollutant. Copper as pollutant (both organic and inorganic) has effect on fish fry and eggs but this effect may be locally devastating but almost harmless to the population as a whole (Haslam, 1991). Environmental factors are responsible for the variation of copper concentration in the aquatic environment. Fish are generally more tolerant than invertebrate. However, the accumulation of copper mostly does not last after the fish have been returned to clean water (Hellawell, 1986).

Effect of Copper on Aquatic Plants

Copper as a trace metal is required for growth and development of aquatic plants but ideal concentration is very low. Copper concentration in the body tissue of aquatic and intertidal plants is detected only 0.01 $\mu\text{g/g}$ which is optimum for their life but beyond this limit copper becomes toxic for plants (Saber, 1997). Accumulation of copper within plants has been found to be higher in the lower parts than in the upper parts (Hossain *et al.*, 1999). The uptake and accumulation of copper by phytoplankton mainly depends on the amount of free cupric ion in the water body. Phytoplankton often assimilates available copper quickly because of their high surface area to volume ratio (Kennish, 1992). Algae usually suffer from severe limitations so It is difficult to assess their copper toxicity. Algae growth may be inhibited at 1 to 2 ppb copper concentration. Among the algae *Chlorella* is more sensitive than *Scenedesmus* (Haslam, 1991). The most frequent measure is the rate of photosynthesis because a decrease in this rate is the primary effects of copper toxicity. Growth reduction to algae is mainly caused by copper toxicity. The uptake of copper by algae appears to be passive but can be influenced by metabolism effects. The mechanism of toxicity is not fully known but is thought to inhibit or slowing the flow of electrons in mitochondrial transfer reactions (Sunda and Guillard, 1972).

When aquatic plants exposed to pollution (copper) may grow poorly - particularly when roots are affected. Due to damage of root system, plants are easily washed out by stream flow. Decreased in root growth and damage are the important of copper pollution, hence loss of aquatic plant species from specific habitat (Haslam, 1991). Diatom communities are also influenced by copper pollution. Some species became flourish at a particular and mild level of pollution. When more sensitive species began to disappear, it means regulation of community occurs only with more severe

pollution (Descy, 1976). Copper concentration in some aquatic macrophytes from a polluted lake is shown in Table 2.

Table 2. Copper concentration ($\mu\text{g/g}$) in aquatic macrophytes from lake Come, Germany.

Species	Copper concentration ($\mu\text{g/g}$)
<i>P. perfoliatus</i>	11.9
<i>P. gramineus</i>	11.8
<i>P. lucens</i>	15.5
<i>P. crispus</i>	12.7
<i>P. pusillus</i>	21.8
<i>M. spicatum</i>	12.4
<i>V. spiralis</i>	25.4
<i>R. trichophyllum</i>	13.3
<i>R. circinatus</i>	15.0
<i>E. densa</i>	19.8
<i>E. canadensis</i>	8.0
<i>N. marina</i>	4.9
<i>C. demersum</i>	35.0

Source: Haslam, 1991.

Toxicity of copper reduces the plant species diversity. Under copper stress, fewer plants occurred and are increasingly confined to the best physical conditions for that plant species. Eventually they are absent from some sites and ultimately diversity drops. The species most sensitive to that pollutant decrease first, the tolerant persisting longer. Therefore the community is increasingly composed of species tolerant to that type and level of pollutant (Kennish, 1992).

Discussion

Metals exhibit a dynamic role in the living system. Metal compounds are used in pesticides raw materials and catalysts energy which end up as residues in food. Information on the distribution and concentration of copper in the organisms and how this trace element is transported to the human through food chain have been shown. Water pollution due to domestic and industrial discharges has already become a great problem in certain regions of the country. The current practices adopted for the discharge of these wastes include direct discharge into watercourses without giving any treatment. Because of increasing industrialization and urbanization throughout the world, the problem of domestic and industrial effluent is constantly on the rise. Human activities and malpractice also contribute a lot in polluting the water courses. The use of fertilizer, pesticides and biocides in the agricultural fields is growing rapidly and ultimately pollutes the water bodies. To maintain the sanctity and purity of the aquatic environment, with the rapid pace of urbanization and industrialization, it is necessary to handle various pollutants in a way so that these will not affect aquatic life adversely. This is a challenging job but needs superlative attention.

Continuous Monitoring Programme: Effective pollution control needs a continuous monitoring of environmental and wastewater characteristics. The monitoring should be done for both wastewater and receiving water. In this regard a schedule for the continuous monitoring of the pollutants in the waste water before and after treatment must be formulated by every industry or public body or to check whether the quality of effluent is within the permissible limits or not.

Waste Water Treatment and Disposal: The basic aim of waste water treatment is to remove the contaminants and pollutants from the waste water so that the treated waste water can be discharged safely into the aquatic environment.

Conclusion

The extent of occurrence or accumulation of copper by aquatic organisms is dependent upon the route of entry i.e. either from surrounding habitat or in the form of food and chemical materials available either in the soil or water sources. In normal life, copper is a part of the dietary requirements of marine organisms. Some enzymes require copper ions as co-factors. In such enzymes, the metal ions may serve one of the two possible roles such as a bridging group to bind substrate and enzyme together through formation of a co-ordination complex or it may serve as the catalytic group.

Water enriched with copper becomes acutely toxic to some organisms, causing change in community composition, sequential effect on prey-predator relationship and reduces photosynthesis rate of submerged plants hence reduction in biomass and cover. As species decrease in abundance, they decrease in biomass, first the more sensitive species then, as dirt worsens, the more tolerant ones. Slightly elevated copper level in natural water may cause histological and morphological changes in tissues; suppression of growth and development; change in biochemistry such as enzyme activity and blood chemistry.

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