

Role of Copper in Environment as a Potential and Challenges

Dharmpal Meet A¹, Rathod Zalak R²

¹Department of Biotechnology, Kadi Sarva Vishwavidyalaya, Gandhinagar, Gujarat, India

²Department of Microbiology and Biotechnology, University School of Sciences, Gujarat University, Ahmedabad, Gujarat, India

ABSTRACT

Copper is a normally mixing component. Present in the world's shell, in seas, lakes and waterways, wellsprings of copper extend from minute follow sums to rich mine stores. Copper is a fundamental component, implying that all plants, fish and creatures need copper to work appropriately. All around the market for copper is one of the biggest of all metals following iron and aluminium. Copper can be delivered into the earth by both characteristic sources and human exercises. Present day life has various applications for copper, extending from coins to colours, and interest for the metal stays high, particularly in industrialized countries.

KEYWORDS: Copper; Microbes; Iron; Aluminium; Metal

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INTRODUCTION

Copper is a naturally stirring element. Present in the earth's shell, in oceans, lakes and rivers, sources of copper range from minute trace amounts to rich mine deposits. Copper is an essential element, meaning that all plants, fish and animals need copper to function properly. (copperalliance.eu) Copper contamination is one of the major environmental hazards in contaminated areas (Chaney *et al.*, 1997). Normal concentration of copper in plant tissues is approximately 5-25 mg/kg. Copper toxicity due to many aspects of its behaviour inhibits iron metabolism and the activities of many enzymes (Hou *et al.*, 2007). Universally the market for copper is one of the largest of all metals following iron and aluminium. The size of the largely market for developed copper is over US\$149 billion every year, Copper has been a material component in the growth of human civilizations for thousands of years. India is one of the top 20 major producers of copper universally. As a result, instability in prices of the metal on the LME has an important bearing on Indian copper trading. Over 30% of India's copper demand comes from the telecom sector and 26% from the electrical sector. In addition, the building and construction, engineering, transport and consumer durables sectors are major consumers of copper in India. (Kabwe; Yiming, 2015)

Environmental form of copper

Copper occurs in the soil almost exclusively in divalent form. The largest fraction of Cu is usually present in the precious stone lattices of primary and secondary minerals. In addition a high fraction of Cu is bound by the soil organic

matter. The Cu ion is adsorbed to inorganic and organic negatively charged groups and is dissolved in the soil way out as Cu²⁺ and organic Cu complexes. Copper is specifically adsorbed to carbonates, soil organic matter, phyllo silicates, and hydrous oxides of Al, Fe, and Mn. (Reed; Martens, 1996) The focus of Cu²⁺ in the soil solution decreases sharply with an increasing pH where as the concentration of organic Cu complex in the soil explanation is less dependent on soil pH. Higher pH may even promote the termination of organic Cu complexes. The divalent Cu ion has a strong affinity to soil organic matter compared with other divalent cations as is shown by the following sequence (Schnitzer, 1965; Skinner, 1967): Cu > Ni > Pb > Co > Ca > Zn > Mn > Mg Copper may be bound in chelated form to organic matter which means that it is held by covalent and coordinative bonds. It is coordinatively bound to O, N, and S atoms following the preference S > N > O. Since N is present in soil organic material in much higher concentrations than S, N atoms take part in the major role in chelating Cu²⁺ in quantitative terms. Recent findings indicate that a large proportion of Cu²⁺ is also bound covalently to carboxylic groups as occur in humic and fulvic acids in soil organic matter and as shown below. This is covalent mono dentate binding of Cu²⁺ to the carboxylic group R-COO⁻ + Cu²⁺ = R-COO Cu⁺ is not as strong as that of the Cu²⁺ chelate. Compared with other divalent cations, it is strong (Me Bride 1989). In this work the bonding strengths of various divalent cations were compared with the bonding strength for Ca²⁺ with three different compounds: humic acid, acetic acid and citric acid. For most of the cation species tested citric acid formed by far

the strongest bonds because of its capability of chelating the cation. Bonding strengths formed by the cations and carboxylate group of acetic acid and humic acid were much weaker. Of all the cation species tested, however, the bonds formed by Cu^{2+} were by far the strongest.

The equilibrium concentration of Cu^{2+} maintained by sparingly soluble Cu^{2+} salts such as carbonates and oxides is higher than the normal levels of Cu^{2+} in the soil solution. The presence of carbonates or oxides in the soil therefore plays no part in restricting Cu^{2+} solubility. The Cu^{2+} concentration in the soil solution is governed by Cu adsorption to organic and inorganic soil particles. For this reason Cu is very immobile in soils and practically not leached in to deeper soil layers. Copper added to the soil as a result of the use of Cu containing sprays or fertilizers is thus largely restricted to the upper soil horizons. (Delas, 1963) The Cu concentration of many soils therefore decreases down the profile. Copper displacement from soils can be brought about either by strong acids or the use of organic compounds which form Cu complexes. The significance of these complexing reagents can be appreciated by the fact that KCN is capable of extracting more than 50% of the total soil Cu whereas non-complexing reagents extract only very small quantities. (Beringer, 1963)

Copper can be released into the environment by both natural sources and human activities. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray. A few examples of human activities that contribute to copper release have already been named. Other examples are mining, metal production, wood production and phosphate fertilizer production. Because copper is released both naturally and through human activity it is very widespread in the environment. Copper is often found near mines, industrial settings, landfills and waste disposals.

Most copper compounds will settle and be bound to either water sediment or soil particles. Soluble copper compounds form the largest threat to human health. Usually water-soluble copper compounds occur in the environment after release through application in agriculture. When copper ends up in soil it strongly attaches to organic matter and minerals. As a result it does not travel very far after release and it hardly ever enters groundwater. In surface water copper can travel great distances, either suspended on sludge particles or as free ions. Copper does not break down in the surroundings and because of that it can accumulate in plants and animals when it is found in soils. On copper-rich soils only a limited number of plants have a chance of endurance. That is why there is not much plant diversity near copper-disposing factories. Due to the effects upon plants copper is a serious threat to the productions of farmlands. Copper can seriously influence the proceedings of certain farmlands, depending upon the acidity of the soil and the presence of organic matter. Despite of this, copper-containing manures are still applied.

MICROBS AND COPPER

Bacterial interaction with surfaces is everywhere in nature. For centuries, human civilizations have used metallic copper in medicine, due to its antibacterial properties, until the start of commercially available antibiotics in 1932. Bacterial interaction is bio corrosion, which is a type of metal corrosion that occurs when microorganisms present in different environments alter metal-solution interface

condition causing a strong interaction that considerably accelerates mechanical failure of metals in a wide range of environments.

UTILIZE OF COPPER

In a natural state, copper is hardly ever found pure (Badiye et al, 2013). The metal is highly conductive of both electricity and heat, and many of its uses take advantage of this quality. Copper can be found in many electronics and in wiring. It is also used to make cooking pots. This metal is also relatively corrosion resistant. For this reason, it's often mixed with other metals to form alloys such as bronze and brass. The metal is closely related with silver and gold, with many properties being shared among these metals. Modern life has a number of applications for copper, ranging from coins to pigments, and demand for the metal remains high, especially in industrialized nations. Many regulars interact with it in various forms on a daily basis. (Badiye et al., 2013) Most copper is used for electrical tools (60%); construction, such as roofing and plumbing (20%); industrial machinery, such as heat exchangers (15%) and alloys (5%). The main long established copper alloys are bronze, brass (a copper-zinc alloy), copper-tin-zinc, which was strong enough to make guns and cannons, and was known as gun metal, copper and nickel, known as cupronickel, which was the preferred metal for low-denomination coins. (Mengel et al., 2018) Copper is ideal for electrical wiring because it is easily worked, can be drawn into fine wire and has a high electrical conductivity. Table 1 shows the Alloys of Cu. (Mengel et al., 2018)

Table: 1 Different alloys mixing with copper

Copper + Zinc = Brass
Copper + Tin = Bronze
Copper + Nickel = Cupronickel
Copper + Aluminium = Aluminium Bronze
Copper + Arsenic = Arsenical Copper
Copper + Tungsten = Copper Tungsten
Copper + Tin + Zinc = Gunmetal

ROLE OF Cu IN PLANT BIOLOGY

The rise of photosynthetic organisms on Earth has driven a progressive addition of oxygen in the environment. This oxidative atmosphere led to a decreased solubility of iron by the formation of iron oxides and to the progressive liberation of soluble Cu (II) from insoluble Cu sulphide salts. (Burkhead et al., 2009) Iron in biological molecules has been gradually substituted by Cu which is able to perform similar functions. This explains why many Cu-proteins have purposeful counterparts that use Fe as cofactor and why growth on a substrate with a toxic Cu level is commonly linked to a decreased Fe-content in roots and leaves. (Burkhead et al., 2009) Plant phenotypes associated with Cu toxicity split similarities with those associated to Fe-deficiency, such as the incidence of leaf chlorosis, decreased leaf chlorophyll substance and enhanced oxidative tension. (Pätsikkä et al., 2002) In contrast, copper deficient plants develop chlorotic symptoms that show first at the tip of the young leaves earlier forming necrotic lesions. Plants grown under Cu deficiency also explain impairment in the photosynthetic transport chain and a reduction in non-photochemical quenching, which is consistent with a lack of plastocyanin (PC) function. (Abdel-Ghany; Pilon, 2008)

In living organisms, the main functions of Cu are the transport of electrons in mitochondria and chloroplasts (the most abundant Cu protein is plastocyanin, a photosynthesis-

related protein involved in the transfer of electrons from cytochrome *f* to P700⁺), they have power over of the cellular redox state (a major Cu-binding protein is the Cu/Zn superoxide dismutase) but also the remodelling of the cell wall (Cohu; Pilon, 2010).

TOXICITY OF COPPER

As Cu deficiency occurs primarily on humus moneyed soils which bind Cu²⁺ strongly, it may be made-up that certain defined organic forms are more readily able to render Cu occupied. (Mengel et al., 2018) Copper is not poisonous in its metallic state but some of its salts are poisonous, especially the most common salts of copper are the Sulphate or the blue vitriol (Nila; Tutia) and the sub-acetate or Verdigris (Zangal). Copper Sulphate is a crystalline salt with blue colour and metallic taste in a small dose of 0.5 g it acts as an emetic but in large doses, as an irritant poison produces gastric and intestinal irritation. Copper sub-acetate is a blue green salt formed by the action of vegetable acids on copper cooking vessels which are not properly lined and which have been used for cooking and storage for a long time. Copper compounds of Arsenic include Scheele's green (Copper Arsenite), Paris green or emerald green (Copper Aceto-arsenite) etc and go by the name "Hirwa" in the local language. Copper is a powerful inhibitor of enzymes. Poisoning effect of copper will commence within 15-30 minutes. (Badiye et al., 2013) Copper toxicity affected the growth of *Alyssum montanum* (Ouzounidou 1994) and Cd of cucumber (Moreno-Caselles et al. 2000) and *Brassica juncea*. (Singh and Tewari 2003) Copper and Cd in combination have affected adversely the germination, plantlet length and number of lateral roots in *Solanum melongena*. (Neelima and Reddy 2002)

COPPER TOXICITY IN PLANT

Although soil hardly ever produces excessive amount of copper on its own, copper toxicity can occur from the repeated use of fungicides that contain copper. Copper toxicity plants appear diminutive, are usually bluish in colour, and eventually turn yellow or brown. Toxic copper levels reduce seed germination, plant vigour, and iron intake. Neutralizing copper soil toxicity is extremely difficult once the problem occurs. Copper has low solubility, which enables it to persist in the soil for years.



Figure: 1 Copper deficient plant

Cu METABOLISM

Copper is taken up by plants mainly through the root system and partly in minor amounts through the shoots and leaves.

(Mattioni *et al.*, 1997) Copper (Cu) is considered as a micronutrient for plants (Thomas et al. 1998) and plays important role in CO₂ assimilation and ATP synthesis. Cu is also an essential component of various proteins like plastocyanin of photosynthetic system and cytochrome oxidase of respiratory electron transport chain. (Demirevska-kepova et al., 2004) Under physiological conditions, the conversion metal Cu is found in the two common forms, the reduced Cu (I) state and the oxidized Cu (II) state. Depending on this state, Cu can bind different substrates. In its reduced form Cu(I) preferentially binds sulphur-containing compounds having a thiol or a thioether group, whereas the oxidized form Cu(II) coordinates mainly with oxygen or imidazole nitrogen groups. (Cohu; Pilon, 2010) This dual chemistry of Cu allows it to cooperate with a large range of molecules, in fastidious proteins, to drive biochemical reaction or stabilize structural features. (Festa; Thiele, 2011) However, being redox active free Cu can directly lead to the generation of reactive oxygen species (ROS) through Fenton chemistry thereby cause damage to proteins, DNA and other bio molecules. (Hänsch; Mendel, 2009)

COPPER DEFICIENCY IN PLANT

Copper is immobile, meaning its deficiency symptoms occur in the newer leaves. Symptoms vary depending on the crop. Typically, the symptoms start as cupping and a slight chlorosis of either the whole leaf or between the veins of the new leaves. Within the chlorotic areas of the leaf, small necrotic spots may form, especially on the leaf margins. As the symptoms progress, the newest leaves are smaller in size, lose their sheen and in some cases the leaves may wilt. The apical meristems may become necrotic and die, inhibiting the growth of lateral branches. Plants typically have a compact appearance as the stem length between the leaves shortens. Flower colour is often lighter than normal. (McElroy et al., 2017) Excess potassium, phosphorus or other micronutrients can indirectly cause copper deficiency. Also if the pH of the growing medium is high, this can induce a copper deficiency as it is less available for plant uptake. (McElroy et al., 2017)

FUTURE ASPECT

- Applications of nonmaterial in agricultural production and crop Protection
- Implication of copper for Phytoremediation
- Use of Copper to made up nanoparticles to the terrestrial plants
- Use of copper as a nanoparticle for controlling the insect, pests and and pathogenic Microbes

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