JBLD, VOL. 19, NO.1&2, 2016, pp. 1-26

Copper in agricultural fields and in crops - a review

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ABSTACT

It is important to understand chemical behaviour of copper in soils so as to comprehend different ways of immobilizing it and avoiding the contamination of the food web. This paper focuses on copper contamination in agricultural soils and in crops grown on copper contaminated soils. Solubility, mobility and bioavailability of copper under different soil conditions as a tool of assessing risks associated with utilization of copper contaminated soils have been discussed. Feasible options that can be used to immobilise/attenuate copper toxicity in soils have been proposed. The presence of elevated concentrations of copper in soils pose ecological risks, therefore, soluble copper should be converted to less soluble fractions. This can be achieved through leaving the land fallow for a long time so as to give soluble copper fractions enough time to change to insoluble fractions. Understanding chemical properties of organic amendments that are added to soils as fertilizers is crucial for avoiding eventual copper mobilization and contamination in soils. The amendments that have a potential of immobilizing copper can be applied on copper contaminated soils as a remedial option. It is recommended to avoid organic amendments that contain elevated levels of copper contents like pig manure.

Key words: contamination, coffee, soils, bioavailability, mobility

INTRODUCTION

Soil is a very important component of ecosystem. It interacts with other spheres, biosphere, hydrosphere, atmosphere and lithosphere (Brady and Weil, 2014). This interaction highlights the importance of managing the soils properly because if the soils are contaminated, there may be a concomitant contamination of other spheres due to the interaction that exists between the soils and the other spheres.

The soil system receives pollutants from natural as well as anthropogenic sources. One of the pollutants is heavy metals due to increased inputs of the metals as a result of different anthropogenic activities. Some heavy metals are toxic even if present in low concentrations and their toxicity magnifies with accumulations in soils, organisms and waters (Bradl, 2004). Elevated levels of available copper in soils and in organisms can lead to copper poisoning and disruption of ecosystems functioning.

Copper is one of the trace elements that have wide economic uses like in the manufacture of fertilizers and pesticides. Since there has been a wide use of this trace element in agriculture, both by large scale and by small scale farmers, it is of prime importance to understand chemical behaviour of copper in soils and its fate in the environment. Research on the relationships between copper concentrations in soils and uptake by crops are not consistent. Strong positive relationships (Brun et al., 2001; Meers et al., 2007; Wang et al., 2003), lack of relationship (Mendoza et al., 2006; Brun et al., 1998; Chaignon et al., 2003; Meers et al., 2007; Wang et al., 2004) as well as weak relationships (Qian et al., 1996; Wang et al., 2004) have all been variably reported. The variability testifies that copper availability to plants is a complex phenomenon, which

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may be plant and or soil specific. Disparities also exist on the uptake and accumulation of copper by different crops and even between varieties of the same crop. For example, Loland and Singh (2004a) reported Cu contents of 842 mg kg^{-1} in bean leaves and 21 mg kg^{-1} in maize leaves. Mzimba (2001) reported up to 1180 mg kg^{-1} Cu concentrations in bean leaves grown on copper contaminated soils in Tanzania where as Senkondo et al. (2014) reported maximum copper concentrations in bean leaves of 14 mg kg^{-1} grown on copper contaminated soils. Loland and Singh (2004a) reported copper concentrations in coffee leaves of as high as 99 mg kg^{-1} in Tanzania while Senkondo et al. (2014) reported a maximum copper concentration of 27 mg kg^{-1} in coffee leaves in Tanzania. The differences on the uptake of copper by different crops is attributable to differences in the copper concentrations in soils (Brun et al., 1998), soil properties (Gandois et al., 2010) and mechanisms of different plants to tolerate elevated levels of copper in their tissues (Li et al., 2009). Differences in extraction methods used by different researchers (Pueyo et al., 2004) and the age of the sampled plant parts can be one of the reasons for the disparities.

Paradox on the relationships between copper concentrations in soils, the uptake and the accumulation by plants and the differences in the copper uptake pattern by different crops and even varieties within the same crop species call for further attention. This work explores the sources of disparities. It specifically analyses the methodologies that have been used by different researchers to assess copper bioavailability and point out the reason for the disparity. The work presents and discusses findings in classic literature. The focus has been on copper dynamics in soils and uptake by crops. It provides up to-date findings on the occurrence of copper in agricultural fields, its interaction with soil components, possible leaching, contamination of the food web and possible ways to immobilise it in soils. Therefore a number of peer reviewed research articles, review papers, books and different legislations were reviewed.

Copper in the environment and agricultural materials

Occurrence and sources of copper in the environment

Copper is the first element in group 1b of the periodic table ranking 26th in abundance in the lithosphere. Copper as a chemical element cannot be degraded. It can only be converted between different physical and chemical forms (Tack, 2010). The usage of Cu by humans has resulted to its elevated quantities in the environment, where copper contents are well above the background levels (Hong, 1996). Copper accumulates in soils mainly as a result of activities such as copper mining and smelting, brass manufacturing, electroplating, continuous atmospheric depositions, application of sewage sludge, municipal composts and pig slurries (Marcato, 2009). Other activities include automotive and industries that produce batteries (Hanafiah et al., 2009) and mineralization and weathering of parent materials containing Cu (Holmgren, 1993).

The use of copper-containing inorganic fertilizers (Fasaei and Ronaghi, 2008), sludge applications, pig manure and copper-based fungicides (Doula et al., 2000; Loland and Singh, 2004a) has grossly increased the concentrations of copper in agricultural fields worldwide. In developing countries, however, the contribution of copper in soils through the application of both organic and inorganic fertilizers may be minimal due to the low usage of the fertilizers. Therefore, the main anthropogenic source of copper in agricultural soils in developing countries is through the application of copper-based fungicides.

Overview of concentrations of copper in agricultural soils

Copper is used for agricultural purposes in fertilizer materials and fungicides. In the United States of America in 1995, about 469,350 kg of copper hydroxide and 51,550 kg of copper sulphate were applied to grapefruit, orange, tangelo, tangerine and temple crops on 259,563 ha in Florida (USDA, 2005).

Copper contamination as a result of heavy use of copper based fungicides has been reported worldwide. Table 1 shows worldwide copper concentrations in copper contaminated soils. Background copper concentration in soils is around 30 mg Cu kg^{-1} soil (Komárek et al., 2009). Other authors report concentrations of between 2 to 50 mg kg^{-1} (Lide, 2009) in uncontaminated soils. Compared to these background copper contents, it is clear that the use of copper based fungicides threatens the ecosystem functioning. Free copper especially Cu^{2+} can affect negatively soil organisms like earthworms (Eijsackers et al., 2005; Helling et al., 2000). However, Lukkari et al. (2005) showed that earthworms living in the copper contaminated area could adapt or acclimatize and continue functioning normally in copper contaminated soils. Norgrove (2007) did not observe adverse effects of copper on earthworms.

Table 1: Concentrations of copper in agricultural fields reported worldwide

Country	Land utilization	Sampling depth (cm)	Copper concentration (mg kg^{-1})	Reference
France	Vineyard	0 – 2	398	Chaignon et al. 2003
France	Vineyard	0 – 3	519	Besnard et al. 2001
Italy	Vineyard	0 – 10	500	Deluisa et al. 1996
Brazil	Vineyard	0 – 5	3215	Mirlean et al. 2007
Czech Republic	Vineyard	11 – 12	168	Komárek et al. 2008
Australia	Vineyard	0 – 1	249	Pietrzak and McPhail, 2004
India			121	Gupta et al. 2008a
Tanzania	Coffee	0 – 20	2300	Mzimba 2001

Microbes are as well affected by elevated contents of copper in soils especially in terms of numbers, activities and diversity (Dumestre et al., 2009). Degradation of organic matter in soils (Dai et al. 2004) is also negatively affected by the elevated quantities of copper. The most affected group of soil microbes are bacteria (Ranjard et al., 2006) because they have low metal resistance (Giller et al., 1998) and as a result of metal persistence in soils, resilience of bacteria may be low thereby affecting ecosystem services. However, Brandt et al. (2010) showed that some soil bacterial communities can exhibit structural and functional resilience to a long term Cu exposure due to their capacity to build up copper tolerance without affecting overall community structure which may be a result of phenotypic adaptation.

Concentrations of copper in agricultural fertilizers

Organic wastes like sewage sludge may contain elevated levels of copper (Zhou and Wong, 2001). When copper containing organic amendments are applied to soils for a long time, the copper contents in the soils may reach elevated levels well over the background levels and lead to its accumulation in soils (Wong et al., 2007; Ashworth and Alloway, 2008) and plant tissues (Gascó and Lobo, 2007; Jamali et al., 2009). However, the chemical speciation of copper added as metal salts or as fungicides is different from the ones introduced by the addition of organic amendments because the amendments may increase the adsorption capacity of the soil thereby decreasing copper mobility in soils (Oliver, 2004). However, Formentini et al. (2015) reported a mobilization of copper as a result of addition of pig slurry to soils. Pig manure contain large quantities of copper because copper is an additive to pig meals (Formentini et al., 2015). Phosphatic fertilizers may contain significant quantities of copper (Nriagu and Pacyna, 1988) as well.

Formentini et al. (2015) found that pig slurry increased exchangeable copper fractions; organic matter bound copper, copper associated with amorphous oxyhydroxides and copper associated with crystalline oxides in soils sampled at 0 – 5 cm depth. However, copper associated with residual fraction did not increase. Therefore heavy use of fertilizer materials containing copper as well as the use of copper based fungicides may grossly elevate copper concentrations in soils well above the background levels. For ecosystem functions and food safety concerns, the uses of such materials need to be regulated in all countries. The fact that some organic manure products may contain elevated quantities of toxic material, several legislative organs worldwide have put restrictions on the use of materials containing elevated quantities of copper. However, the critical copper concentrations in soils differ from one legislation authority to another depending on the purpose of the legislation (EU, 2008). For example, copper toxicity thresholds varied approximately 3 orders of magnitude (3 - 2,400 mg copper kg^{-1}) among soils. Total copper contents in sewage sludge of different European Countries ranged between 190 and 641 mg Cu kg^{-1} dry matter (EU, 2008). The European Union (EU) warning and critical legislative limits for the concentrations of copper in sewage sludge has been set at 50 and 140 mg kg^{-1}, respectively, at pH ranges between 6 and 7 (Council of the European Communities, 1986).

Why copper-based fungicides in plantations?

Copper based fungicides have been widely used in coffee plantations to control coffee berry diseases and coffee leaf rust caused by *Colletotricum coffeanum* and *Hemeleia vastatrix*, respectively, (Matthews et al., 2003) in Arabica coffee. These diseases are mainly controlled by the use of copper-based fungicides like Kocide 101, Funguran and Blue copper (Dickinson et al., 1984) and other organic fungicides. In East Africa, the fungicides that are effective in controlling CBD include the copper containing formulations, 50% copper as well as ortho-difolatan, daconil, benlate, topsin, tecto 60, delan and du-ter (Vine et al., 1973a). Copper fungicides, du-ter, difolatan, benlate and daconil were available for the control of CLR. However, of all these fungicides, only the copper based fungicides effectively controlled both CBD and CLR (Vine et al., 1973b).

Good efficacy, broad spectrum of activity and relatively low cost of copper-based fungicides (Masaba, 1998) and the plant nutritional advantage of the copper (Patrício et al., 2008), has for a long time made the widespread use of copper-based fungicides in East Africa justifiable. When it rains, these fungicides are washed away and deposited on soils. In addition, excess chemicals drop on the soils when the pesticides are being applied. Repeated applications of the fungicides cause high accumulations of copper in the soils (Loland and Singh, 2004a). In contrast, in Brazil, Patrício et al. (2008) reported that copper oxychloride was less effective in controlling coffee leaf rust compared with organic pesticides; hence it is being sprayed once per growing season mainly for fertilization purposes and to control dieback.

Copper-based fungicides like the Bordeaux mixture, $CuSO_4$ + $Ca(OH)_2$, Cu $(OH)_2$, and Cu_2O have been widely used to control vine fungal diseases, such as downy mildew caused by *Plasmopara viticola*. Apart from vineyards and coffee, Cu-based fungicides are used to control fungal diseases in hop fields, apple and avocado orchards (Epstein and Bassein, 2001) and in the cultivation of several vegetables like tomatoes and potatoes. Copper from copper-based fungicides as a result of routine fungicides application can add up to 3 – 4 kg ha^{-1} with a single application. Though the amounts deposited at a time during the application may be very small, long term application may lead to elevated levels of copper in the soil (Zhang et al., 1997; Valladares et al., 2009).

Masaba (1998) reviewed the epidemiology and chemical control of the fungal pathogens in coffee in East Africa. He reported that the CBD fungus needs free water and temperatures ranging between 15^{o}C and 25^{o}C to germinate and develop. The development of CBD is highly linked to the coffee growth pattern. The CBD attacks berries within four to 16 weeks after flowering. Thereafter, the fully grown green berries are resistant, but they become susceptible again at the ripening stage. Because coffee growing areas receive bimodal rainfall, coffee plants experience two flowerings per annum. Since it takes nine months from flowering to maturity, coffee crops overlap and therefore, in one year there are four critical periods that dictate the use of fungicides to protect the crop. Therefore, to combat the CBD, at least four sprays are needed per growing season. If not controlled, CBD can cause up to 80 % of crop loss (Javed, 1982). The CLR develops under similar conditions as CBD but needs optimal temperature range of between 15^{o}C and 28^{o}C. The CLR infestation does not develop under direct sun light, but when coffee trees are shaded by trees or banana plants.

Heavy use of copper-based fungicides has resulted in the elevated levels of copper in soils and threatens ecosystem functioning. Therefore the use of copper-based fungicides to control diseases should be stopped because their continual use would worsen the situation. Other fungicides which are not copper-based and that do not persist in the soil environment should be adopted. The price of organic fungicides is relatively higher than the ones for copper-based products. It is recommended that respective governments actively support the use of alternative fungicides. Another plausible alternative is to use plant varieties that are resistant to the fungal diseases. In Tanzania, the Tanzania Coffee Research Institute (TaCRI) as a research institution responsible for coffee research has developed such resistant varieties. However, the pace of replacing the old, susceptible varieties with the new, resistant ones is still slow due to limited financial resources, facilities and low adoption rate by the small scale farmers.

Risks of contamination of food web by copper in agricultural farms

Copper as a trace metal accumulates and persists in the soil environment. Part of it can be in available forms and part may exist in unavailable forms (Brallier, 1996) depending on soil conditions (Sauvé et al., 2000) and the time of contact between the applied copper and the soil (Lu et al., 2005). There is a risk that part of the available copper can be taken up by the plants and transferred to the food web thereby posing health risks (Lamb et al., 2009). High concentrations of copper in soils may cause phytotoxicity to plants. Following concerns of high concentrations of copper in soils, it is recommended that the concentrations of copper in vineyard soils that exceed 60 mg kg^{-1} require further investigation (Rusjan et al., 2007). Some crops may take up excess quantities of copper and contaminate the food web. Table 2 depicts different copper concentrations as reported by different authors.

Table 2: Copper concentration in different plants and plant parts

Plant	**Plant part**	**Country**	**Cu concentration (mg kg^{-1})**	**Reference**
Cocoa	Green leaves	Nigeria	1435	Adeyeye et al., 2006
Banana	Green leaves	Nigeria	286	Adeyeye et al., 2006
Chinese cabbage	Leaves		119	Xiong and Wang, 2005
Lettuce	Leaves		136	Inaba and Takaneka, 2005
Coffee	Leaves	Tanzania	991	Loland and Singh (2004a
Maize	Leaves	Tanzania	21	Loland and Singh (2004a
Bean	Leaves	Tanzania	842	Loland and Singh (2004a

The hazards of using copper-based fungicides for coffee production are relatively limited because coffee is a deep-rooted crop. Because copper in soils tends to be rather immobile, its high concentrations are found only within 10 cm of the top soil (Loland and Singh, 2004a: Komárek et al., 2009) and also concentration of copper in coffee beans is as low as 16–17 mg kg^{-1} (Dickinson et al., 1984). Therefore the risk of contaminating the food web is higher for shallow rooted crops like beans and vegetables that are grown in line with coffee in copper contaminated soils, if the crops can take up substantial quantities of copper. Despite the copper immobility in the soil, sometimes small contents may be leached to lower parts of the soil profile (Payne et al., 1988) as a result of movement of organic-complexed copper (Loland and Singh, 2004b).

The bioavailability of copper is a subject of concern due to the fact that it is associated with a number of health problems such as dermatitis and various types of cancer. It causes damages to heart, kidney, liver, pancreas and brain. Furthermore, it is associated with intestinal distress and anaemia (Al Rub et al., 2006). Excess copper accumulates in the liver, brain, pancreas and myocardium (El Bayaa et al., 2009). Elevated copper contents in soils cause phytotoxicity. For example, copper has been associated with phytotoxicity in crops such as dill (Zheljazkov, et al., 2006), durum wheat (Michaud, et al., 2008), and barley (Ali et al., 2004). Total Cu contents of 322 mg kg^{-1} caused phytotoxicity to barley grown on Cu-contaminated forest soil (Ali et al., 2004). It has been observed that Diethylene triamine pentaacetic acid (DTPA)– extractable Cu exceeding 200 mg kg^{-1} caused copper phytotoxicity to *Portulaca oleraceae* (Deepa et al., 2006). A concentration of 400 mg kg^{-1} of copper caused phytotoxicity to citrus plants (Alva et al., 1999). Other detrimental effects of excessive quantities of copper include reduced bioavailability of iron by plants, culminating in stunted growth and inhibition of growth of fine roots in maize plants (McBride, 2001). Despite the toxic effects of copper at elevated quantities, copper is one of the micro-nutrients essential for plants (Gupta, et al., 2008; de Santiago et al., 2008) as well as animals (Marschner, 1995) and it is involved in a number of physiological processes. If deficient, adverse effects are observed in both plants and animals. However, due to its abundance in soils, copper deficiency in human is seldom reported. But in sandy, light textured soils with low background copper contents or strong Cu-binding peat soils the bioavailability of copper may be low (Alloway, 2009) and lead to copper deficiency to plants. Under such circumstances, Copper deficiency will mainly affect young leaves and reproductive organs and typical symptoms are twisted or malformed leaves, chlorosis or even necrosis (Marschner, 1995).

Most risk assessment studies use total metal concentrations as a measure of risks associated with heavy metals in soils. However, this method presents little information on the quantity of the heavy metals that is bioavailable (Lu et al., 2005; Fangueiro et al., 2005) because total copper concentration incorporates the soluble as well as insoluble fractions of copper. Most studies on the influence of aging on availability of copper to plants were done in laboratories using recently spiked soils. The spiked soils are incubated for a month, or a few months, and copper extractability as a measure of its availability, is then determined (Jalali and Khanlari, 2008). This approach does not give full information on the long term availability of heavy metals as influenced by aging. For example, Senkondo et al. (2015a) did not find any significant difference on copper concentrations in bean shoots as a result of differences in total copper load and exchangeable copper in soils. They further found no significant difference on copper uptake by bean shoots between long-term contaminated soils and recently copper spiked soils. This indicates that the total copper load in soils and the aging effect had no control over the bioavailability of copper to bean shoots. Therefore spiking soils with copper salts and incubate them for a few days and carryout solubility studies without carrying out bioavailability studies can grossly exaggerate the level of risks of copper that would be taken up by plants. They concluded that the joint effects of soil properties and plant factors may have played a major role in restricting the excessive uptake of Cu than the aging effect or the total copper load.

Chemical forms of copper in soils

Copper has two oxidation states, Cu (I) and Cu (II). Monovalent copper is mainly found in anaerobic environments. It can be oxidized to Cu (II) under oxic environments. Copper (II) is considered to be a more toxic form because it is more mobile and reacts with a number of soil constituents (Hall and Anderson, 1999). Copper in the soil exists in different forms such as water soluble, exchangeable, organically bound, that associated with carbonates, hydrous oxides of Fe, Mn, Al and residual forms (Sauvé et al., 2000; Tack, 2010). Chemical forms of Cu determine its availability and fate in soils. The distribution of copper into these species is dependent on soil properties such as redox potential (Eh), CEC, texture, oxides content and clay mineralogy (Sims, 1986). Other factors include pH, ionic strength and concentration of dissolved organic matter (Degryse et al., 2009).

Copper has high affinity for organic matter which provides specific binding sites for copper in the soil (Karlsson et al., 2006; Tack, 2010). When copper is introduced to the soil, it undergoes processes such as chemisorption, ionic exchange, complexation with organic matter, adsorption, and may be occluded in carbonates or oxide minerals or in the structure of primary and secondary minerals (Hickey and Kittrick, 1984). In the soil pore water, copper binds to dissolved organic matter, for example fulvic or humic acids. The complex between copper and these organic acids may mobilise or immobilise copper depending on soil conditions. Fulvic acids may increase copper mobility when complexed with copper because it is soluble in water, while humic acid may form insoluble complexes, although the humic acids may also form soluble complexes, depending on the degree of dissociation of the humic molecules (Gondar et al., 2006). Copper mobility may be enhanced through increasing pH as a result of an eventual increase in dissolved organic matter fraction and an increase in its copper affinity with increase in soil pH (Tyler and Olsson, 2001). But in general, the association of Cu with these organic ligands indeed deters copper mobility (Bradl, 2004). In organic acids, Cu is bound to $–NH_2$, SH and –OH (Alloway, 2009).

Copper has different affinity to different soil constituents. The adsorption preference of copper for soil constituents is: Mn oxides > organic matter > Fe oxides > clay minerals. However, in general, soil organic matter forms specific copper adsorption in soil and is the main constituent responsible for retaining the sorbed Cu and it (organic matter) may bind up to 98 % of soluble copper (Sauvé et al., 1997). Literature shows that the type, property and the contents of organic matter in soils will determine the solubility, mobility, bioavailability and toxicity of copper in soils. Under anoxic conditions, copper reacts with sulphides to form insoluble compound, CuS, thereby limiting its mobility.

Vertical distribution and downward movement of copper in soils

Copper in soils is rather immobile (Pietrzak and McPhail, 2004) but in some cases it can move vertically downwards in the soil depending on its speciation (Mirlean et al., 2009). Its movement is governed by soil physico-chemical properties and the interaction between the properties (Gomes et al., 2001) and tillage practices (Payne et al., 1988). The copper solubility increases with a decrease in soil pH (Sims and Kline, 1991) and it increases with increase in copper-soluble complexes in soil solution (Planquart et al., 1999). In calcareous soils, most copper is mainly restricted within the 10 cm of top soil (Komárek et al., 2009) and therefore immobilised. The downward movement of Cu is limited in clay soils due to low hydraulic conductivity and the sorption of Cu. Clay minerals often carry negative charges; therefore the high valence cations are held and retained by negatively charged soil colloids. Zhang and Lo (2008) concluded that $CuSO_4$ addition to irrigated soils for over 10 years at an application rate of 18.7 kg $CuSO_4$ ha^{-1} $year^{-1}$ was not likely to cause significant Cu groundwater pollution. However, few reports have shown downward movement of copper which resulted to underground water contamination. For example, significant vertical migration of copper has been reported in southern Brazil in an area characterised by acid sandy soils with an average precipitation of 1300 mm/year (Mirlean et al., 2009).

In soils that received copper-based fungicides for 63 years, higher concentrations of copper over the background levels were encountered only within 30 cm, suggesting limited downward movement of copper (Senkondo et al., 2015b). Limited mobility of copper in soils coincided with the high levels of organic carbon and CEC (Fan et al., 2011). They therefore considered fallowing as a good management option to halt copper mobility in copper contaminated soils. In the same study, the background copper concentrations in copper contaminated soils but left fallow for over 20 years had background copper concentrations just below 10 cm. This phenomenon was attributed to the fact that the soluble fractions of copper had enough time to revert to less available forms due to aging effect. In an abandoned copper contaminated soils in Czech Republic, the highest copper concentrations was observed in an abandoned vineyard soils where no tillage or any other activities are carried out that would mobilise copper (Komárek et al., 2008). The authors contended that if the soils are reused for agricultural production of food crops, there will be a danger of contaminating the food web.

The mobility of heavy metals is reduced considerably in unsaturated soils (Zhang and Lo, 2008) causing the solubility and migration of copper under low soil water content to be very limited. This explains why heavy metals are retained within the surface soils in arid regions. In their copper leaching experiment, they showed that most copper was retained on the upper 1 cm, and the concentrations decreased with soil depth. However, such high concentrations of copper found within the root zone may pose a risk of contaminating the food web. It can be concluded therefore that downward movement of copper in copper contaminated soils is generally very low because it forms very stable complexes with organic matter and other soil constituents. Hence the likelihood of contaminating underground water resources as a result of leaching is very low.

Factors affecting copper mobility in soils

Soil physical-chemical properties and their effects on leaching of copper

The movement of water and dissolved heavy metals in soils is affected by soil physical properties such as soil texture (Deng et al., 1998), soil porosity, bulky density, infiltration rate of water in the soil, the interaction between soil colloids and the infiltrated water and the hydraulic properties of the soil (Zhang and Lo, 2008). Up to 88% of the added copper was held within the top 2 cm depth of the soil profile in clay soils (Zhang and Lo, 2008). Clayey soils immobilize copper than sandy soils (Richards et al., 2000). If the hydraulic properties of the soil allow water movement, the transport of copper can be significant in soils (Richards et al., 2000).

Zhang and Lo (2008) performed a study to model the movement of copper dissolved in water in three dimensions. Vertical penetration depth was more significant than horizontal movement, and the increase in soil density was effective to retard the movement of copper. They further reported that clay content had a strong influence on the transport of copper. A small difference in clay content can result in a significant difference in copper migration. Rodriguez-Rubio et al. (2003) reported that copper was more retained in the silt fraction than in sand and in clay fractions because organic matter in soils is preferentially accumulated in the silt fraction. Senkondo et al. (2015b) found a significant positive relationship between silt fraction and copper concentration at different soil layers in copper contaminated soils.

Soil pH is an important factor in determining the distribution of copper over different chemical forms and ultimately determines its solubility and availability. In acidic conditions copper becomes more soluble (Martínez and Motto, 2000; Pueyo et al., 2004), with the exchangeable forms and organically bound forms becoming dominant (Sims, 1986). Gupta and Aten (1993); Chaignon et al. (2003)

and Mitchell et al. (1978) noted a negative correlation between soil pH and the bioavailability of copper. However, Sanders et al. (1986) did not observe effects of soil pH on copper bioavailability at pH values between 5 and 6 signifying that other soil properties may be important in determining the copper mobility. Under alkaline conditions, copper is largely precipitated (Alva et al., 2000). However, Lexmond and van der Vorm (1980) showed that increasing the pH can rather increase the bioavailability and toxicity of Cu to plants. Sauvé et al. (2000) reported that Cu solubility in the soils was a resultant of pH, the total metal burden and organic matter contents. The concentrations of ionic copper decrease with time because copper binds to soil constituents (Kunz and Jardim, 2000). Bibak (1994) observed a 75% increase in copper adsorption on metallic oxides when the pH changed from 6 to 7. However, Inaba and Takenaka (2005) found no difference in bioavailability of copper to lettuce under different pH conditions.

Carbonates can have effects on copper solubility either directly through their surface interactions or indirectly through their effects on soil pH and other soil constituents (Martínez and Motto, 2000). Other soil chemical and mineralogical properties such as iron and aluminium oxides, mineralogy and redox potential, or the combination of all (Scotti et al., 1998; Clemente et al., 2003; Tack et al., 1996), redox potential of soils (Charlatchka and Cambier, 2000), and soil texture (Otte et al., 1991; Vig et al., 2003) have a great influence on the bioavailability of copper. Senkondo et al. (2014) reported a significant positive relationship between soil electrical conductivity and concentrations of copper in bean leaves. If the properties of the soil do not favour increased bioavailability of copper, cultivation of food crops can continue without contaminating the food web. On the contrary, if the soil physico-chemical conditions favour increased solubility and bioavailability of copper, there is a high risk of polluting the food web (Bozkurt et al., 1999; Mårtensson et al., 1999; Seeda et al., 1997; Jacob and Otte, 2004).

Effects of organic matter and other soil constituents on solubility, mobility and bioavailabilty of copper

Organic matter content is one of the factors that determine the bioavailability of copper in soils (Gomes et al., 2001; Gupta and Aten, 1993; Brun et al., 2001). Organic matter in soils can bind as high as 49% of the total copper contents in soils (Nóvoa-Muñoz et al., 2007) and therefore organic matter plays a significant role in copper immobilization in soils. For soils amended with organic matter, copper tends to accumulate on the top few centimetres due to the high affinity of copper to form inner sphere complexes (Srivastava et al., 2005; Formentini et al., 2015). Organic matter upon decomposition release humic acids and fulvic acids. Humic acids, depending on soil pH (Walker et al., 2004) form stable complexes with metals (Park et al., 2011) which will eventually result in lower phytotoxicity (Karlsson et al., 2006). When copper in soils is stabilised by Organic matter, its availability, mobility, toxicity and transfer to other ecosystems is lessened (Kumpiene et al., 2008; Park et al., 2011: Li et al., 2009; Silvetti et al., 2014). On the other hand, fulvic acids react with copper to form soluble Cu-organic matter complexes that are soluble and consequently enhance copper mobility and uptake by plants (Almås et al., 1999; Bengtsson et al., 2006; Pérez-Esteban et al., 2012) or transfer it to water resources (Alloway, 2009; Schwab et al., 2007). Organic matter influences copper solubility through its influence on soil pH. For example, Pérez-Esteban et al. (2012) reported a significant reduction in exchangeable copper fraction when sheep-horse manure was applied to mine soils. In the same soils, exchangeable copper fractions were increased when pine bark amendments were applied. The difference was attributed to the effects of the amendments on soil pH. The sheep-horse amendments increased soil pH while the pine bark amendments lowered soil pH. Furthermore, the sheep-horse manure had higher proportion of humic acid and lower proportion of fulvic acids where as the pine-bark amendment had higher proportion of fulvic acid. Kaschl et al. (2002) observed that complexing properties of different organic fractions of MSW compost vary with their humic character and chemical composition.

Other studies have reported that organic amendments added to soils may not have any effect on metal mobility. For example, studies on the effects of sewage sludge compost in copper contaminated vineyard soils (Korboulewski et al., 2002; Businelli et al., 1996) who studied the influence of repeated application of composted municipal solid waste on a calcareaous soils did not show any significant effect on copper mobility. The effects of composted organic waste applications on the mobility and migration of trace metals in soils depend on the total loads of organic matter and metals, their properties, and the properties of their association with the amended soil (Cambier et al., 2014).

Wang and Staunton (2006) studied water extractable copper by following the composition of soil water extracts in straw or leaf treatments in reduced or aerated environments. They observed 10-fold differences in the proportion of water-extractable copper, depending on conditions of incubation. They concluded that a single measurement cannot give an estimation of Cu mobility in soil (Wang and Staunton, 2006). It is therefore clear that organic amendments added to soils may either enhance or deter copper availability depending on chemical properties of the amendment in question. Therefore, before using any organic amendment in copper contaminated soils, care should be taken. Chemical properties of the amendment in question, chemical and physical properties of the soils where the organic amendments are going to be applied must be studied. Furthermore, copper mobilization/immobilization studies should be carried out well in advance. Otherwise the mobility of copper may be enhanced and aggravate a problem of metal toxicity in soils and in biota. Contents of $CaCO_3$ in soils have an influence on copper solubility. For example, less copper was retained by $CaCO_3$ when organic matter was increased in soils signifying a competition between the two (Saha et al., 1991). However in acidic soils, the contribution of carbonates on copper binding may be negligible.

Most of studies on the mode of occurrence, biological and physicochemical availability, mobilization and transport of copper from organic amendments have been conducted in temperate soil–climate conditions (Legros et al., 2013; Formentini et al., 2015). Since climate is of paramount importance for biogeochemistry of heavy metals in soils, it is important to carryout studies that will explore mobilization of copper contained in organic amendments and their effects on native copper in soils under tropical and subtropical climatic conditions.

Aging and copper availability

The term “aging” describes the processes by which the extractability, bioavailability and toxicity of copper added to soils decrease with time (Lu et al., 2005). The solubility and availability of heavy metals in soils is low as compared with other metals in soils because soil constituents adsorb the heavy metals. When copper is added to soils it undergoes reactions which lead to immobilization or formation of compounds that are insoluble (Jalali and Khanlari, 2008). This elucidates that the difference in bioavailability or toxicity of copper between long-term copper contaminated soils in field and freshly added copper to soils in a laboratory differ greatly. It is therefore of prime importance and of necessity to understand the aging processes in ecological risk assessment of metals in soils (Zhou et al., 2008). The time period of contact, or the residence time, between the added metals and soil components may affect the solubility and availability of copper. With time, metals and soil constituents undergo reactions such as complexation, adsorption, exchange, chelation, and precipitation or diffusion into the mesopores and macropores of soils (Tack, 2010). These reactions may lead to the alteration of highly soluble species into insoluble or less soluble ones (Brallier et al., 1996). Although it is assumed that aging reduce solubility, mobility and bioavailability of copper, very few studies have been carried out to explore whether and how time effects influence metal bioavailability (Bataillard et al., 2003; Davies et al., 2003). Most studies on the effects of aging on copper solubility, mobility and bioavailability have been undertaken in test tubes where adsorption isotherms of the soils are developed.

Furthermore, fractionation of copper in to different fractions to determine the distribution of copper species as affected by incubation time is studied after the soils are spiked with copper salts. For example, in a study carried out by Lu et al. (2005), soils were incubated for a few weeks and fractionation analyses were carried out. The information obtained from such studies may not give true information on whether the mobile fractions are really bioavailable to plants. A study by Senkondo et al. (2015a) revealed that there was no significant difference on copper uptake by *Phaseolus vulgaris* grown in recently copper spiked soils with high contents of exchangeable copper fractions and a long time copper contaminated soils with lower contents of exchangeable copper fractions. This signifies that without carrying out uptake studies by plants, there is a possibility of exaggerating the risks associated with the presence of copper in soils. Copper bioavailability to plants is mainly controlled by the joint effects of soil properties (Brun et al., 2001; Gandois et al., 2010) than the aging effect or the total copper load. Silvetti et al., (2014) commented that the uptake studies by rye grass were the best method in assessing bioavailability of metals. Studies comparing copper uptake from soils which have been contaminated by copper for a long time, uncontaminated soils, and recently spiked soils is hardly found in the literature. It is recommended that uptake studies should utilise contaminated soils and if possible under field conditions in order to assess the actual bioavailability of copper.

Copper extractability, concentration and uptake by plants

Single extraction methods and sequential extraction methods are used to assess heavy metal behaviour and phytoavailability in soil. The following single extraction methods have been proposed in different countries (Meers et al., 2007). 1M NH_4NO_3 (Germany), 0.1M $NaNO_3$ (Swiss) and 1M CH_3COONH_4 (France). $CaCl_2$ extraction which is widely recommended single extraction method gives an indication of easily mobile and available fraction (Kabata-Pendias, 1993) but underestimates the potential availability of copper in soils as compared with other extraction methods like EDTA. EDTA extraction method may yield up to 100 fold-higher copper concentrations than $CaCl_2$ extraction method (Komárek et al., 2008). Asada et al. (2012) and Filgueiras et al. (2002) commented that environmental risk is related to the transport of mobile and potentially mobile fractions. Therefore the $CaCl_2$ extraction method is the best method for risk assessment. However, Komárek et al. (2008) found that the $CaCl_2$-Cu extraction method is not a good predictor of copper bioavailability in slightly alkaline vineyard soils.

Nitric acid (Tipping et al., 2003) measures geochemically active metals where as 0.1 M HCl (Fiszman et al., 1984) measures metals that can be released under moderate acid attack. *Aqua-regia* extraction method gives an indication of total copper load. Although the *aqua-regia* extraction method gives an indication of total copper contamination, it is not a good tool for the determination of potential risks from soils and sediments contaminated by metals (Qian et al., 1996; Rieuwerts et al., 1998; Pietrzak and McPhail; 2004) Fernández-Calviño, 2009; Lu et al., 2005) because it extracts even copper fractions that cannot be remobilised under normal soil conditions.

The most commonly used methods to determine the nature of the soil solution and the ability of the soil to replenish metals are those which use chelates such as EDTA (Merry et al., 1986) which were shown to be useful in predicting plant metal deficiencies, but they do not seem to correlate very well with metal toxicity in plants. DTPA extraction methods have also been used to assess metal availability (Lindsay and Norvell, 1978). The solution is buffered at pH 7.3 and therefore it excludes effects that are associated with carbonates dissolution.

While strong correlations between plant growth and chelator extractant tests have been reported at toxicity levels, the relationships obtained have generally only been applicable to a single soil type (Plenderleith and Bell, 1990). There has been contradicting reports on the relationship between the extractable copper in the soil and the concentration of copper in plants. Likewise the suitability of different single extraction methods on predicting the bioavailability of copper to different plant species has not been standardised. Furthermore, different extraction methods yield different results.

The interpretation of these results in association with the possible toxicity to biota needs harmonisation. Table 3 shows a range of methods that have been used in copper extraction. The existence of so many methods makes it very difficult to compare results from different extraction methods. It is therefore of utmost importance to harmonise the extraction methods so as to be able to use and compare information for risk assessment.

Table 3: Relationship between the concentration of copper using different extraction methods and the concentrations of copper in different plants and different plant parts

Extraction method	**Test crop**	**Plant part**	**Type of relationship**	**Reference**
DTPA	Corn	leaves/ grains	Non	Payne (1988)
DTPA	*Phaseolus vulgaris*	Shoots	Positive	Meers (2007)
0.05 M $CaCl_2$	*Lactuca sativa*	Shoots	Positive	Aten and Gupta (1996)
0.01 M $CaCl_2$	*Phaseolus vulgaris*	Shoots	Positive	Meers (2007)
0.01 M $CaCl_2$; DTPA, EDTA, CH_3COONH_4	*Zea mays*	Shoots	Positive	Brun et al. (2001)
DTPA, EDTA, NH4OAc	*Zea mays*	Roots	Positive	Brun et al. (2001)
0.01 M $CaCl_2$	*Apium graveolens*	Shoots	Positive	Wang et al. 2004
0.01 M $CaCl_2$	*Spinacia oleracea*	Shoots	Positive	Wang et al. 2004
0.01 M $CaCl_2$	*Brassica compestris*	Shoots	Non	Wang et al. 2004
0.005M DTPA, 0.01M CaCI2, 0.1M	*Brassica compestris*	Shoots	Non	Wang et al. 2004
0.005M DTPA, 0.01M CaCI2, 0.1M	*Brassica compestris*	Shoots	Non	Wang et al. 2004
0.005M DTPA, 0.01M CaCI2, 0.1M TEA	*Brassica compestris*	Shoots	Non	Wang et al. 2004
1 M NH_4NO_3	*Phaseolus vulgaris*	Shoots	Positive	Meers (2007)
1 M $MgCl_2$	*Phaseolus vulgaris*	Shoots	Positive	Meers (2007)
1 M NH_4OAc (pH = 7)	*Phaseolus vulgaris*	Shoots	Positive	Meers (2007)
0.5 M HNO_3	*Phaseolus vulgaris*	Shoots	Positive	Meers (2007)
0.1 M HCl,	*Phaseolus vulgaris*	Shoots	Positive	Meers (2007)
CH_3COONH_4-EDTA	*Phaseolus vulgaris*	Shoots	Positive	Meers (2007)
Aqua regia	*Phaseolus vulgaris*	Shoots	Positive	Meers (2007)
Aqua regia	*Triticum turgidum duram L.*	Shoots	Positive	Michaud et al. (2007)
Aqua regia	*Lycopersicon esculentum*	Shoots	Non	Chaignon et al. 2003
Aqua regia	*Lycopersicon esculentum*	Roots	Positive	Chaignon et al. 2003
0.5M CH_3COONH_4, 0.5M HAc, 0.02M EDTA (pH 4.65)			Positive	Komárek et al. (2008)
0.5M CH_3COONH_4, 0.02M EDTA (pH 4.65)	*Triticum turgidum duram L.*	Shoots	Positive	Michaud et al. (2007)

As a consequence of lack of harmonisation protocols, different researchers have come up with different methods that suitably predict the bioavailability of copper to different plant species. For example, Brun et al. (2001) showed that $CaCl_2$ extraction method gave the best prediction of bioavailable Cu to *Zea mays* shoots as compared to CH_3COONH_4, EDTA and DTPA extraction methods, while Komárek et al. (2008) found that the EDTA extraction method is more suitable for predicting the potential availability of copper in soils.

Michaud et al. (2007) showed that EDTA-extractable copper correlated better with copper concentrations in plants than the total copper contents but they proposed that the 0.05 M EDTA should be regarded as a method of assessing the potential bioavailability and not the actual availability because it extracts more copper than the plants may be able to extract and hence exaggerating the bioavailability. In other words, EDTA is an aggressive extraction method hence can exaggerate the actual availability. Other researchers have some reservations on chelating extractants. Bell (1986) reported that chelating extractants fail to correlate well with plant toxicity for several reasons. At toxic levels, the metal concentrations may exceed the chelating ability of the extractant. This makes such methods insensitive to increases in metal contents. This fact may account for the lack of correlation between the concentrations of EDTA extractable copper in soils and the concentrations of copper in plant tissues reported in literature. Studies show that there is little correlation between plant shoot copper and total soil copper for maize, suggesting that maize plants have a strong barrier to copper transfer from roots to shoots (McBride, 2001). Therefore, total soil copper concentration may have little significance to copper bioavailability and toxicity. These contradicting reports on the relationship between the concentrations of copper in soils and the concentrations of copper in different plants shows that the bioavailability and the uptake of copper by crops is soil-or plant-specific and that risk assessment should be on specific plant or on specific soils basis.

Although the use of single extraction methods has widely been used to assess the extractability of heavy metals in soils, they have a number of limitations. Their limitations lie in the lack of consistency in the different procedures used. Consequently, the results obtained are operationally defined depending on the experimental conditions used (type and concentration of extracting agent, soil mass: volume ratio, shaking time and speed of shaking) (Pueyo et al., 2004). This reality makes data linkage tricky and hampers the standardisation of these methods. To date, there is no generally accepted method of estimating the bio-availability of heavy metals in soils (Pueyo et al., 2004). To be able to harmonise soil extraction methodologies on heavy metal extraction (copper inclusive), it is of paramount importance to gather sufficient information on the performance of the available extraction procedures in different soil-types. However, there are too many single extraction methods available in literature that make it difficult to harmonize phytoavailability studies in soils and enable the results obtained from the methods to be compared. This may be one of the reasons for the contradictory reports on the relationship between the concentrations of extractable copper in soils and the concentrations of copper in plants. Furthermore, most risk assessment studies did not include plant uptake studies which would indicate if the extractable copper using the protocol would correlate with the concentrations of copper in the plants. Studies by Pueyo et al. (2004), Meers et al., (2007) are among the commendable studies that have attempted to compare soil extraction methods in an attempt to harmonise soil extraction methods for risk assessment studies. However, more data from different areas are needed to be able to come-up with a reliable methodology.

Most of the bioavailability studies use the bulk soils to measure the copper concentrations. It has been shown that root exudates in the rhizosphere can change completely the chemistry of the rhizosphere soils and make it behave completely different from the bulk soils (McLaughlin et al., 1998). This may completely change the bioavailability status of copper (Hinsinger, 2001). It is a well known fact that plant roots take-up water, nutrients and pollutants that are in contact with plant roots. The methodology of using the bulk soil in assessing the bioavailability of copper in soils may be one of the reasons of the reported disparities on the relationship between copper contents in soils and the concentrations of copper in plants. Chaignon et al. (2002) reported that in acidic soils, rhizosphere soils were made alkaline while in alkaline soils, the rhizosphere soils were made acidic in tomato and oilseed rape.

Sequential extraction methods are used for fractionation studies to give an expression of easily available copper fractions, potentially available fractions and inert fractions (Pietrzak and McPhail, 2004). There are two widely used sequential extraction methods, the BCR extraction procedure (Bureau Communautaire de Référence (Rauret et al., 1999)) and the procedure proposed by Tessier et al. (1979). However, the methods have a lot of limitations such as non specificity nature of reagents used, formation of various complexes, redistribution and precipitation during extraction (Song et al., 1999). Furthermore, a problem arises when different extraction methods are used and results compared (Komárek et al., 2008). There is lack of adequate methods that allow an unambiguous determination of the forms of association of copper with a given soil fraction. Chemical methods available are being criticized because of technical drawbacks like non-selectivity of the extraction solutions or artefacts as a result of Cu re-distribution during extraction process (Besnard et al., 2001).

Another research gap on the methodologies of estimating bioavailability studies is the plant part that should be sampled for bioavailability studies. Some studies have recommended roots as a good plant part to assess bioavailability (Brun et al., 2001; Alva et al., 1993). while studies by (Meers et al., 2007; De Abreu et al., 1996; Haq et al., 1980; Gupta and Aten, 1993) used aerial plant parts in assessing the metal bioavailability. Assessing bioavailability based on root analyses may exaggerate the risks of contaminating the food web and may not be relevant especially if the consumable parts of the plant are leaves, seeds or fruits. Furthermore, influence of the age of a plant part that should be sampled for bioavailability assessment has received little attention. There is no standard age that the plant in question should be sampled for bioavailability studies. For example, Meers et al. (2007) showed that the strength of relationship between extractable copper in soils and the concentrations of copper in bean leaves differed as a result of age of the plants tested. For example, the coefficient of relationship between concentrations of copper in soils and the concentrations of copper in bean shoots for two weeks was 0.52 while for the concentrations of the bean shoots grown for four weeks, the coefficient of relationship was 0.81. It is now evident that the two weeks plants showed a weak relationship while the four weeks plants showed a very strong relationship. Plants that have transpired more have a chance of accumulating higher metal contents than plants that transpired less. The type of plant digestion method can also affect the strength of relationship. For example, in the same study by Meers et al. (2007), the authors found a coefficient of relationship between $CaCl_2$ extractable copper in soils and the concentrations of copper based on dry weight in bean shoots grown for four weeks was 0.39 but when the relationship was based on ash weight a coefficient of relationship of 0.81 was observed.

Different growth media have also been used in studies on the bioavailability of copper. For example pot experiments utilising soils (Brun et al., 2001), hydroponic cultures (Trujillo-Reyes et al. 2014). This makes the comparison of data obtained under field conditions, pot experiments under very controlled conditions and the ones from hydroponics system difficult.

Copper deficiency and toxicity to plants

Copper is an essential micronutrient for both animals and plants. However, it can be toxic to the organisms if present at concentrations approximately 10–50 times higher than the required concentration (Hall et al., 1999). Jones (1972) reported that the normal concentrations of copper in different plants range between 3 and 40 mg kg^{-1}. Deficiency of copper in plants like citruses cause dieback while excess of copper in the plants causes chlorosis (Alva et al., 2000). Plants grown on soils contaminated with copper may show the toxicity signs including decreased leaf, stem and root dry weights especially on acidic soils but on alkaline soils the effects may not be noticed (Alva et al., 2000). The toxicity of copper to any particular crop depends very much on the type of soils and management factors. In other crops, however, copper phytotoxicity has been reported for example in vineyard, temperate and tropical orchards (Besnard et al., 2001).

Borkert et al. (1998) reported threshold copper toxicity for maize tissues as being 20 to 21 mg kg^{-1}. Above this critical concentration, toxicity effects show up. Shainberg et al. (2001) reported that a copper concentration in bean leaves of 23 mg kg^{-1} caused a 20% decrease in chlorophyll content as compared with the plants with 12 mg kg^{-1} copper content. They further reported that a copper concentration of 23 mg kg^{-1} in *Phaseolus vulgaris* induced oxidative stress and inhibition of *Glutathlone reductase*. Coffee seedlings grown on solution containing 10 mg kg^{-1} copper had severely distorted and impaired root systems as well as leaf and shoot necrosis (Aduayi, 1972). Symptoms of copper toxicity under field conditions have not been proven and coffee appears to be tolerant of elevated copper levels in soils and in tissues (Dickinson and Lepp, 1985).

Legislation on the use of copper contaminated soils and organic materials

Due to detrimental effects of copper on ecosystem functioning and on the potential danger of contaminating the food web, developed countries have restricted the use of copper contaminated soils and copper contaminated organic amendments for crop production. Based on soil properties and analytical procedures, European Union has defined the permissible levels of metals (including cooper) in agricultural soils above which the soils are considered contaminated (Kabata-Pendias and Pendias, 2001) and the Netherlands government have set up metal limits in soils above which an intervention is required (Adriano et al., 1997).

Abatement options

Copper is a potentially hazardous trace element if it is excessively bioavailable. There must be strategies to halt its mobility in soils. Many options are available in literature like excavation and offsite deposition (Alloway, 2009), phytoremediation (Vymazal, 2013) and onsite stabilization (Stuckey, 2008; Sakar et al., 2007). Excavation is feasible if the area is small and it just transfers the problem from one place to another and may be expensive. For phytoremediation, it may take about 500 years to bring concentration to background levels for some metals if the soils are highly polluted and therefore the method is not feasible because of such a very long waiting time.

The most feasible way of managing copper toxicity is the attenuation of its mobility and bioavailability in soil by manipulating soil properties like raising the pH of the soil. This can be achieved through the application of liming materials. A plausible alternative that is feasible even by small scale farmers in their coffee fields in developing countries is by adding soil amendments such as organic matter for the purpose of increasing the copper binding capacity of the soils (Lombi et al., 2010; Silvetti et al., 2014). Most amendments used for onsite remediation have got high quantities of Fe/Al/Mn amorphous and/or crystalline oxy-hydroxides that can deter the trace elements (copper inclusive) bioavailability through sorption reactions (Violante et al., 2008). However, the limitation of adjusting soil pH is that it may be a temporary solution because soil pH may decrease depending on the soil management. This may change copper mobility status. It is therefore important to continuously monitor soil pH and adjust it accordingly.

Organic amendments like cattle manure has a potential to immobilise copper (Loland and Singh, 2004b). Again with depletion of organic matter, copper may be released to the soil solution and become mobile (Alloway, 2009). It is therefore advisable to monitor the levels of organic matter contents in copper contaminated soils and replenish it accordingly to continue to keep the copper immobile. Another management option is to leave the soils uncultivated for a couple of years to let the copper revert to species that can not be easily mobilised. Komárek et al. (2008) reported low copper mobility in copper contaminated land that was left uncultivated for a long time as compared to other copper contaminated farms that were under constant tillage. It is possible to make use of organic amendments by small scale farmers because the materials are locally available and are cheap.

Concluding remarks

Copper is an essential nutrient for plants as well as animals. However, it may become toxic if taken excessively. The chemical species of copper present in soils together with the soil physical, chemical and mineralogical properties, the total copper load and the interaction among the properties determine the fate of the metal in soils. Therefore copper bioavailability in soils is not governed by a single soil parameter. The bioavailability and the uptake of copper by crops is soil-or plant-specific and that risk assessment should be on specific plant or on specific soils basis. Solubility, mobility and plant availability of copper in agricultural soils under normal soils conditions is limited. Copper mobility in soils may occur under extreme soil conditions like low pH. Extreme lowering of soil pH can occur if, for example, there is excessive depletion of $CaCO_3$. Downward movement of copper in copper contaminated soils is generally very low because it forms very stable complexes with organic matter and other soil constituents. Hence the likelihood of contaminating underground water resources as a result of leaching is very low. Leaving contaminated soils undisturbed for a long time makes copper to revert to forms that are immobile.

Despite immobility of copper in soils, for ecosystem functions and food safety concerns, the uses of organic fertilizer amendments containing elevated quantities of copper need to be regulated in all countries. It is therefore important to stop the use of copper-based fungicides in agricultural fields. Alternative chemicals that do not persist in the environment for a long time can be adopted to control fungal diseases instead of copper based fungicides. Additionally, the adoption of plant varieties that are resistant to the fungal diseases should be given priority through intensification of extensions programs.

The most important finding in this review is that although aging and the total copper load have been reported in most literature to play a significant role in attenuating or intensifying the toxic effects of copper in soils, these properties may not affect copper bioavailability to some crops in some soil types. Therefore, copper bioavailability is soil and plant specific. It is therefore plausible to conclude that risk assessment studies on the potential danger of contaminating the food web should be carried out on specific plants and soils.

Too many extraction methods in use make it difficult to harmonize phytoavailability studies in soils for risk assessment studies. This makes the interpretation of the results obtained from the methods to be inconsistent culminating in the contradictory reports on the relationship between the concentrations of extractable copper in soils and those in plants. Single extraction methods used to assess the extractability of heavy metals in soils have a number of limitations such as the lack of consistency in the different procedures used. This makes data linkage tricky and hampers the standardisation of these methods.

RECOMMENDATIONS

Some organic amendments enhanced copper mobility while some deterred it. Therefore, before using any organic amendment in copper contaminated soils, mobilization/immobilization behaviour of the amendment and of the soils in question must be studied before the amendments are applied. Most of studies on the mode of occurrence, biological and physicochemical availability, mobilization and transport of copper from organic amendments have been conducted in temperate soil–climate. Climatic variability can affect biogeochemistry of heavy metals in soils. It is therefore important to carry out copper biogeochemistry studies in tropical and subtropical regions

Although it is assumed that aging reduce solubility, mobility and bioavailability of copper, very few studies have been carried out to explore whether and how time influences metal bioavailability. Furthermore, most studies on the effects of aging on copper solubility, mobility and bioavailability have been undertaken in laboratories and the soils incubated for a short time. The information obtained in such studies may not represent actual field conditions on whether the mobile fractions are really bioavailable to plants or not. It is therefore recommended that future studies on aging effects on copper mobility be carried out using the soils which have been naturally contaminated under field conditions so as to get a true picture of copper bioavailability.

A number of methods are available for copper extraction in soils. The existence of so many methods makes it very difficult to compare results from the different extraction methods. It is therefore recommended to harmonise the extraction methods so as to be able to use and compare the information for risk assessment. To date, there is no generally accepted method of estimating the bio-availability of heavy metals in soils. Efforts should be directed towards harmonising extraction methodologies on heavy metal extraction (copper inclusive). This will be achieved through gathering of sufficient information on the performance of the available extraction procedures in different soil-types from different areas.

Limits on the concentrations of copper in agricultural soils or organic amendments above which agricultural production of certain crops must be stopped are non-existent in Tanzania. Tanzania and other developing countries ought to put in place such legislations.

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