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Effect of Soil pH, Cattle Manure and Total Copper Load on Copper Solubility in Copper Contaminated Soils

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

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ABSTRACT

Coffee fields in Kilimanjaro, Tanzania have been contaminated with copper (Cu) as a result of long term use of Cu-based fungicides. Solubility and mobility of Cu in soils may be detrimental to the environment and human health due to possible leaching thereby contaminating underground water resources. Cu solubility and bioavailability to plants may decrease with time through conversion of the contamination to less available forms, a process referred to as 'aging'. Therefore, this study explored the interaction effects of soil pH, cattle manure and the total Cu load on Cu solubility in long term Cu contaminated soils. Soils treated with and without cattle manure were leached with water adjusted to pH levels of 4, 5, 6 or 8.5. The results revealed that Cu solubility was higher in soils with higher total Cu load and that cattle manure had varied effects on Cu solubility at different pH levels. The soils buffering capacity were adequate enough to arrest fluctuations in soils pH and therefore acid rains as well as over liming may not cause excessive solubility of Cu in long term Cu contaminated soils.

Keywords: Solubility; copper; soil pH; cattle manure and total copper load.

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1. INTRODUCTION

Due to increased reliance on Cu based fungicides in controlling fungal diseases in coffee farms worldwide, there has been a public concern about the accumulation of Cu in the soils and its potential leaching into underground waters, leaving the plant with less available forms in the soil [1]. International interest on the fate of metals in contaminated soils is increasing due to both direct possible toxicities to biota and indirect toxicities to human beings through contamination of groundwaters and accumulation of these toxic metals in the food web [2].

Reports on the solubility and mobility of Cu in soils differ from one study to another. Some studies have shown that metals in the soils are immobile [3-7] while some studies, for example, Kaschl et al. 2002 [8] revealed that metals in soils are mobile. The disparities in the reports of these studies stemmed out from differences in the soil physical and chemical properties and the total Cu load [9], organic matter and soil pH [10]. Low Cu solubility and mobility in soils has been ascribed with the formation of insoluble Cu-humic substances, which render the metal immobile [11]. In other study enhanced Cu leaching has been attributed to the formation of soluble Cu-dissolved organic carbon (DOC) complexes [12].

Organic manure contains minerals that can improve nutritional status of soils and can improve soil physical, biological and chemical properties [13]. However, the added organic matter may enhance metal solubility [10]. For example, 17 times increase in Cu leaching after the addition of compost manure has been reported [11]. On the other hand, organic matter applied to soils may deter metal solubility through the formation of insoluble organo-metal complexes [14] and therefore reducing the risk of contaminating underground water resources.

Under alkaline conditions, Cu may be soluble because the bonds that hold organic matter to metals are disrupted and acidic components of organic matter are converted to their soluble salt forms. Soluble organics thus increase a carrying capacity of soil solutions for metals at elevated pH values by forming soluble metal–organic complexes [15]. However, it has been reported that major fractions of Cu in the calcareous soils in Florida were held in quite stable forms, which prevented leaching [16]. The study of Richards et al. [17] shows that there is no significant increase in Cu concentration after leaching the silty clay loam soils treated with sludge, even at high pH values. Other study reported that soil acidification reduced solubility of trace metals as a result of the reduced organic matter solubilization under acidic conditions [18].

Environmental risks can unexpectedly showup themselves within a short duration in response to slow changes in a chemical environment over time [19]. For example, the exhaustion of free $CaCO_3$ in metal contaminated environment might cause a decrease in soil pH with perhaps one unit or more [19]. Following the changes in soil pH, there may be a concomitant abrupt and strong increase of trace element contents in the soil solution to which the ecosystem is not adapted. Such a possibility for unanticipated alterations in the behaviour of pollutants has been termed as a “chemical time bomb’’ [20]. As a result of air pollution by industries, acid rains have been reported in Ivory Coast [21]. Acid rains of pH as low as 4.35 - 5.7 have also been reported in South Africa [22]. The rains may significantly lower the soil pH and affect the solubility, bioavailability and leaching behavior of Cu in Cu contaminated soils. On the other hand, the potential danger that is inherent in the Cu contaminated farms may be the solubilization of Cu which may be accelerated by the occurrence of acid rains. Therefore, the effects which acid rains may have on Cu solubility in Cu contaminated soils ought to be studied in order to include the information to be gathered in risk assessment initiatives.

As with the increased legislation on soil contamination by heavy metals, there is an increased demand for methods of risk assessment [23]. Some studies have proposed sequential extraction methods for risk assessment, especially for the potential solubility and mobility of metals in metal contaminated soils [24,25]. In European countries, the use of batch experiments as methods of risk assessment in metal contaminated soils is increasing [23]. Moreover, for the study of the leaching behavior of metals, batch [26] and column experiments [23,27] have been employed. Bishop et al. [28] showed that different organic wastes have different effects on the solubility of elements. However, there is little information on the soil interaction between organic amendments, total Cu load and the soil pH at which the solubility of metals increases or decreases. Moreover, results reported by other workers emphasized the lack of universal formula for predicting Cu solubility and leaching in the soils. Therefore, the solubility behavior of metals in soils is soil specific. If a soil is contaminated by metals, leaching behavior of metals in that soil and the conditions that may deter or enhance the solubility of metals ought to be studied. The paradoxical phenomena on Cu mobility in Cu contaminated soils reported by different researchers, suggest the need of investigations on long term Cu contaminated soils. Most studies on the solubility of metals involve spiking the soils with metal salts which are incubated for a few weeks before carrying out leaching tests. This type of a methodology may be proper for assessing risks in soils that have recently received heavy dose of metal contaminants from sources like industrial spills. However, in agricultural soils that have been receiving small doses of metal contaminants like Cu, but for a long time (more than 50 years), the methodology of spiking soils with metal contaminants may overestimate the risks of enhanced Cu mobility because the Cu will not have long enough time to interact with soil constituents, like the situation in coffee fields where the equilibrium time may be longer than 50 years. At least 10 years are needed to attain stabilization between metals and soil constituents [29]. Therefore, risks of Cu mobility associated with drastic changes in soil conditions should utilise soils that have been contaminated right from the field, and not recently Cu spiked soils.

The present work studied the effects of (CM), pH of leaching water and the total Cu load, as well as their effects on the solubility of Cu in two types of long term (more than 50 years) Cu contaminated soils in a batch experiment. The ability of the soils to resist changes in pH in relation to Cu solubility was explored in the current study.

2. MATERIALS AND METHODS

Two contaminated soils from Cu contaminated coffee farms were used in this study. One type of soil was collected from MS Rural district (MS), and another type was collected from MW district (MW) in Kilimanjaro, Tanzania. The soils collected from MW are classified as Humic-Umbric Acrisols while the soils collected from MS are classified as Eutric Nitisols [30] according to FAO system of soil classification [31]. Soils collected from MW have been receiving Cu based fungicides for 50 years and the farmer is still using Cu-based fungicides. Soils collected from MS had been receiving Cu-based fungicides for 63 years but the farmer stopped using the Cu based fungicides 10 years ago. After the soils were dried and passed through a 2 mm sieve, each soil type was mixed with 5% w/w of cattle manure (CM). The samples were then mixed with 25% (w/v) of water and equilibrated for 30 days. The treatments were replicated four times. The treatments in the experiment have been presented in Table 1. At the end of the incubation, batch experiments were carried out as follows;

Distilled water adjusted to pH values of 4, 5, 6 or 8.5 was added to the soils at 1:10 soil: water ratio and shaken in a mechanical shaker for 24 hours. The low pH water in this study was selected to mimic the acidic condition that may be caused by acid rain, and the high pH values were selected to imitate alkaline conditions that may be caused by over-liming.

Table 1. Experimental batch conditions used in the study

Treatment number	Soil type	CM	Water pH
1	MS	-	4
2	MS	-	5
3	MS	-	6
4	MS	-	8.5
5	MS	+	4
6	MS	+	5
7	MS	+	6
8	MS	+	8.5
9	MW	-	4
10	MW	-	5
11	MW	-	6
12	MW	-	8.5
13	MW	+	4
14	MW	+	5
15	MW	+	6
16	MW	+	8.5

MS=Moshi soil; MW=Mwanga soil, CM=cattle/cow manure

During the shaking process, pH values were determined but only pH values after 24 hours have been presented. The samples were filtered and the concentrations of Cu in the filtrate were determined by Scientific Atomic Absorption Spectrometer, Buck 205, USA. The selected physical and chemical properties of the soils which were used in the study are presented in Table 2.

The (CM) used in the experiment had aqua regia extractable Cu of 11 mg kg^{-1}, and $CaCl_2$ extractable Cu of 0.5 mg kg^{-1}, an EC of 9.6 mS

Table 2. Physicochemical properties of soils used in the study

Sampling location	pH	OC (%)	CEC ($cmol_{(c)}$ kg^{-1})	Total Cu (mg kg^{-1})	K^+ ($cmol_{(c)}$ kg^{-1})	Ca^{2+} ($cmol_{(c)}$ kg^{-1})	Mg^{2+} ($cmol_{(c)}$ kg^{-1})	Sand (%)	Silt (%)	Clay (%)
Mwanga	5.8	3.8	30	200	2.5	11	0.5	26	28.8	45.2
Moshi	5.9	4.5	42	984	4.3	20	4.3	18	18.8	63.2

cm^{-1} and a pH value of 8.6. At pH levels of 4, 5, 6 and 8.5, respectively, Cu concentration in the CM was 4.4, 1.4, 2.2 and 1.4 mg kg^{-1}. Laboratory analysis was carried out at Selian Agricultural Research Laboratory situated in Arusha, Tanzania.

As a quality control measure, standard solutions were prepared from standard metal stock solutions (Merck, Darmstadt, Germany) and used for calibration. Each replicate sample was analyzed in duplicate and averages calculated. Calibration was carried out after every 20 samples. One standard was being analyzed after 10 samples. The Analysis of variance (ANOVA) was carried out to examine the differences ($p = 0.01$) on the concentrations of Cu among the treatments using S PLUS 8.2 software (Insightful Inc., USA). The Tukey's method ($p = 0.05$) was used to compare the means between the treatments.

3. RESULTS

3.1 Influence of Cattle Manure on Cu Solubility

For the soils collected from MS, CM had varied effects on Cu solubility. In CM treated soils, the manure did not show any significant effect on Cu solubility at pH 4 and pH 8.5, whereas at pH 5, Cu concentration in CM treated soils was significantly lower as compared to the corresponding treatment that did not receive CM. However, at pH 6, CM treated soils had significantly higher Cu concentration than the corresponding soil that did not receive the cattle manure. For MW soils, CM did not have any significant influence on Cu solubility (Table 3).

3.2 Cu Solubility in Relation to pH of the Leachate Solution

Despite the fact that the leaching water in the experiment was adjusted to pH values between 4 and 8.5, the leachate solution remained well buffered and there was no wide variation of leachate pH. In general, CM slightly increased the pH of the leachate by 0.1 to 0.6 pH units and therefore the pH of the leachate solution was not very much affected by the addition of the manure. For soils collected at MS, CM unamended soil, Cu solubility was significantly low at leachate pH of 5.68; and the solubility significantly increased at pH 5.87 but the solubility decreased at pH beyond 5.87 (Fig. 1). The trend of the curve reveals that if the pH of the solution increases, Cu solubility would decrease. As for MS, CM amended soils, the trend of Cu solubility was similar to that in unamended soils; but the difference is that in CM amended soils, the significantly high Cu solubility was observed at two pH values, namely 5.96 and 6.79 forming an 'n' shaped curve (Fig. 2). If the curve is extrapolated, the increased pH of the solution would result to a decrease in Cu solubility.

Table 3. Influence of cattle manure on Cu solubility

CM untreated soils		CM treated soils	
Treatment	Cu (mg kg^{-1})	Treatment	Cu (mg kg^{-1})
MS pH 4	16.75[a]	MS pH 4+CM	12.7[a]
MS pH 5	31.1[a]	MS pH 5+CM	25.6[b]
MS pH 6	20.5[b]	MS pH 6+CM	24.7[a]
MS pH 8.5	16.6[a]	MS pH 8.5+CM	13.4[a]
MW pH 4	4.8[a]	MW pH 4+CM	8.4[a]
MW pH 5	7.1[a]	MW pH 5+CM	7.2[a]
MW pH 6	9.7[a]	MW pH 6+CM	7.9[a]
MW pH 8.5	4.5[a]	MW pH 8.5+CM	3.3[a]

The values are averages of four replicates. Values followed by the same letters in the same row are not significantly different according to Tukey's method of means comparison (p=0.05).CM= cattle/cow manure; MW = Mwanga soil; MS = Moshi soil

Soils collected from MW, unamended soils had a significantly low Cu solubility at leaching pH value 5.37; and a significant high Cu solubility was attained at pH values of 5.75 and 5.98. However, Cu solubility dropped significantly at pH values beyond this range, forming an inverted 'v' shaped curve (Fig. 3). The extrapolation of the curve reveals that with increased solution pH, Cu solubility would continue to decrease.

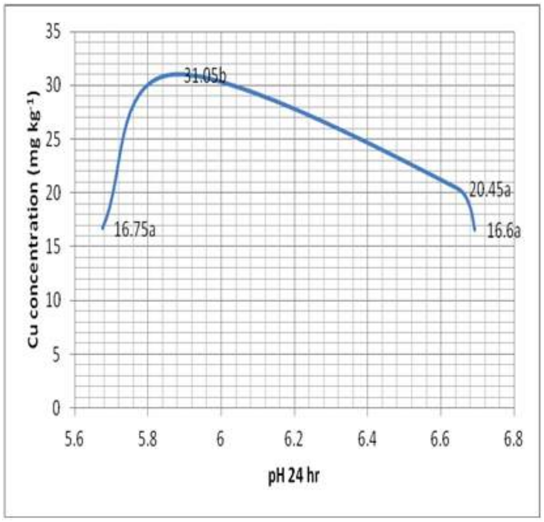

Fig. 1. Relationship between the concentration of Cu and leachate solution pH for Moshi unamended soil

The same letters show that the values are not significantly different according to Tukey's method of means comparison (p=0.05)

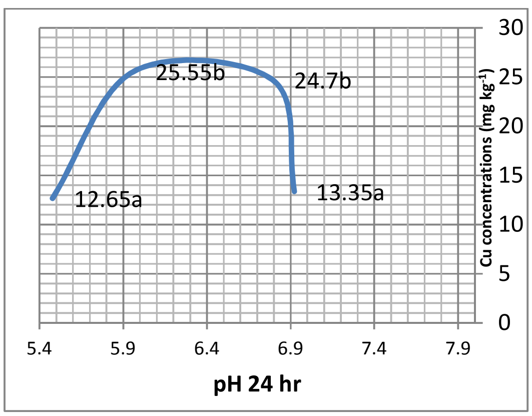

Fig. 2. Relationship between the concentration of Cu and solution pH for Moshi CM amended soils

The same letters show that the values are not significantly different according to Tukey's method of means comparison (p=0.05)

A significantly higher Cu solubility was obtained at pH 5.76 and 6.79 and significantly low concentrations were obtained at pH 6.25 and 6.83 for the MW, CM amended soils (Fig. 4).

4. DISCUSSION

4.1 Changes in Soil pH and Cu Solubility

Soil pH is one of the most central soil parameters that affects the solubility and mobility of metals in soil solution [32]. High soil pH leads to a deterred Cu mobility as a result of the formation of precipitates, due to an increased number of adsorption sites, decreased competition between Cu and H^+ for adsorption sites and the enhanced Cu associations with humic substances [33,34]. The soils used in the study were well buffered and therefore they resisted wide variations in pH as evidenced by the pH of the leachate water (Table 4) compared with their original pH values (Table 2). This shows that even if the areas receive acid rains of pH values of as low as 4, the soils will maintain the pH values at relatively higher values thereby deterring changes that would be experienced if the pH of the soils were reduced to extremely low values due to the acid rain.

Cu solubility was enhanced at soil pH values between 5 and 6 because of the formation of soluble organo-Cu complexes [27]. This is in line with the findings of the present study. In controlling Cu mobility in MS soils using the cattle manure, the pH of the soils must be taken into consideration. A combination of cattle manure and pH values in an alkaline range immobilised Cu in the present study.

The results on Cu solubility in the present study for MS soils contradict with the general reported information by other scholars [2,3] who observed higher Cu solubility under low soil pH conditions. The difference in the solubility may have stemmed from the fact that in the present study, the Cu contamination was a result of an intermittent addition of Cu through the application of Cu-based fungicides culminating in decades of equilibration between the Cu added and the soils, whereas in other studies the soils were spiked with Cu salts and equilibrated for 40 days giving lower equilibration time. Under such conditions of low equilibration time, Cu will be in free forms in solution or in easily exchangeable forms. The free Cu forms become more soluble with decreased soil pH [15]. Where as in the present study, the equilibration time was more than 50 years after the first applications of the Cu-based fungicides, most Cu could have been converted to more unavailable forms [35]. Studies have shown that 10 years period is needed to allow slow equilibration of the organo-mineral adsorption and complexation processes to stabilize the metal activity [29]. This shows that the solubility behavior of free Cu and that of Cu which has been bound to different soil fractions may be different.

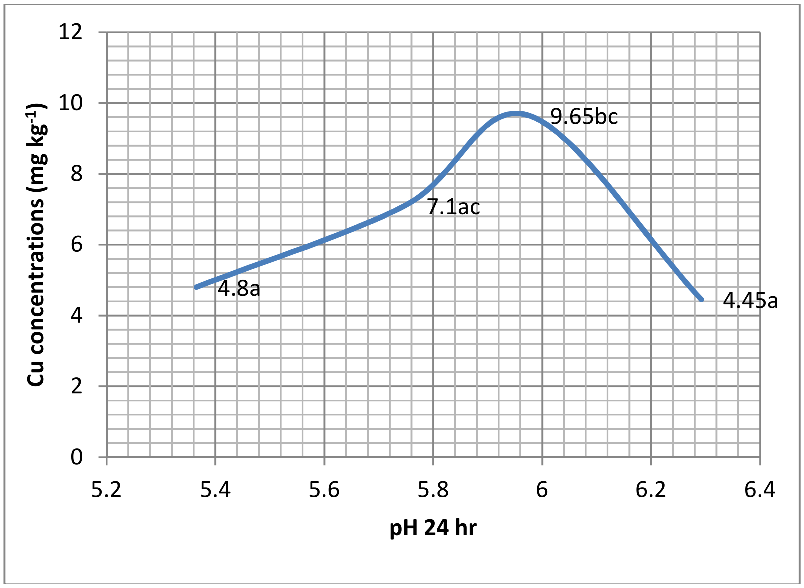

Fig. 3. Relationship between the concentration of Cu and solution pH for Mwanga unamended soil

The same letters show that the values are not significantly different according to Tukey's method of means comparison (p=0.05)

Table 4. pH of leachate solution in the treatments

Moshi soils		Mwanga soils	
Treatment	**pH 24 HR**	**Treatment**	**pH 24 HR**
MS pH 4	5.68	MW - pH 4	5.37
MS pH 5	5.87	MW - pH 5	5.75
MS pH 6	6.65	MW - pH 6	5.98
MS pH 8.5	6.69	MW - pH 8.5	6.29
MS + CM - pH 4	5.48	MW + CM - pH 4	5.76
MS + CM - pH 5	5.96	MW + CM - pH 5	6.25
MS + CM - pH 6	6.79	MW + CM - pH 6	6.79
MS + CM - pH 8.5	6.92	MW + CM - pH 8.5	6.83

The values are averages of four replicates. Values of different letters in the same row are significantly different according to Tukey's method of means comparison (p=0.95).MS = Moshi soils; MW = Mwanga soils

Table 5. Comparison in Cu solubility between the two soil types

Moshi soils		Mwanga soils	
Treatment	**Cu (mg kg^{-1})**	**Treatment**	**Cu (mg kg^{-1})**
MS pH 4	16.75^{a}	MW pH 4	4.8^{b}
MS pH 5	31.05^{a}	MW pH 5	7.1^{b}
MS pH 6	20.45^{a}	MW pH 6	9.65^{b}
MS pH 8.5	16.6a	MW pH 8.5	4.45^{b}
MS pH 4+CM	12.65^{a}	MW pH 4+CM	8.4^{b}
MS pH 5+CM	25.55^{a}	MW pH 5+CM	7.15^{b}
MS pH 6+CM	24.7^{a}	MW pH 6+CM	7.9^{b}
MS pH 8.5+CM	13.35^{a}	MW pH 8.5+CM	3.25^{b}

The values are averages of four replicates. Values followed by the same letter in the same row are not statistically significant different according to Tukey's method of means comparison (p=0.05).MS = Moshi soils: MW = Mwanga soils

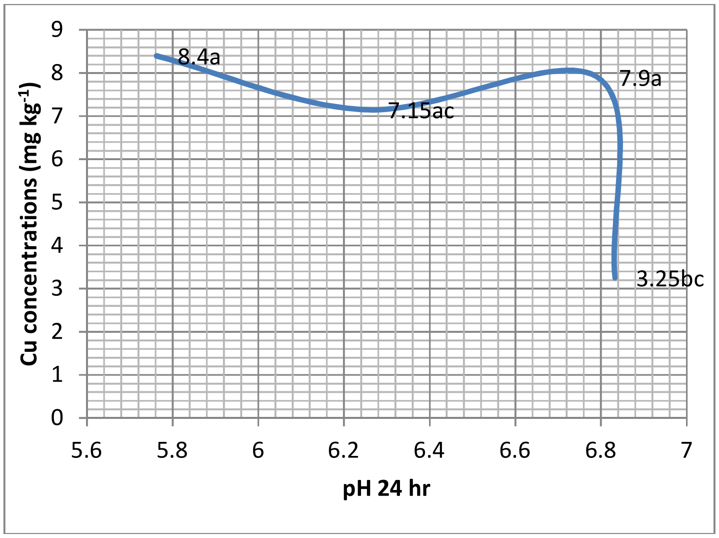

Fig. 4. Relationship between the concentration of Cu and solution pH for Mwanga CM amended soil

The same letters show that the values are not significantly different according to Tuk ey's method of means comparison (p=0.05)

In risk assessment, care should be taken to predict Cu mobility by including the length of time the soils have been in contact with Cu. This is due to a converse phenomenon observed whereby Cu solubility was reduced under the most acidic conditions in the present study especially with soils collected from MS. Unfortunately, no information in literature was found on Cu solubility from soils of similar contamination history for comparison purposes. MW soils untreated with cattle manure exhibited a sharp fall in Cu concentrations with increased soil pH (inverted ''v'' shaped curve) as compared to the corresponding soils collected from MS, which had an ''n'' shaped curve. MW soils had significantly lower contents of organic carbon than MS soils. The higher organic matter contents may have imparted relatively higher Cu retention over a wider range of pH in soils collected from MS. Organic matters in soils are well known for their high cation exchange capacity. In coherence with these observations, cattle manure treated soils had an ''n'' shaped curve, elucidating that Cu solubility is relatively stable over a wide range of pH in the presence of cattle manure.

4.2 Influence of Cattle Manure on Cu Solubility in Moshi Soils

The dissolved organic carbon precipitates with a decreased soil pH [36] and its solubility would increase with increase in soil pH. Soil acidification reduces solubility of trace metals as a result of the reduced organic matter solubilization which leads to reduced mobilization of metals under such acidic conditions [18]. Cattle manure may have as well influenced Cu solubility through alteration of soil pH. The solubility of Cu to a large extent is governed by its binding to humic substances in the solid and dissolved phases [23]. Cu forms very stable complexes with humified organic matter and these metal formed complexes with humic acids are less soluble under acidic conditions [34]. In coherence with the results of the present study, other studies have demonstrated that high soil organic matter content coincided with high metal retention capacity [10]. This fact explains the reduced Cu solubility in leaching water at pH value of 8.5 in the present study.

Pig slurry amendments influenced the characteristics of soil humic substances [37]. [37] observed a decrease in contents of acidic functional group and alterations of the corresponding affinity for ion (H^+) binding. This shows that such alterations can have a significant influence on transport of trace elements and macronutrients as well as toxic metals in soils. In line with these findings, cattle manure in the present study altered the solubility behaviour of Cu. It is therefore safe to conclude that metal complexing characteristics of soil organic matter is a mechanism that explains the position of the organic matter as either sink or source of trace elements in soils.

Organic matter is composed of fulvic acids and humic acids [38]. These two important organic acids have a profound effect on Cu binding behavior of a soil. Chemical species of Cu which are present at a particular pH level of the soil determine the solubility of Cu [39]. When studying Cu binding to fulvic acid, the authors found that free Cu^+ increased with a decrease in soil pH and the Cu binding to fulvic acid decreased with an increase in soil pH. In a theoretical model that predicted the Cu binding to fulvic acid, it was observed that Cu bound to carboxylic groups of fulvic acid reached its peak between pH 5.5 and 6.5 where as under neutral to alkaline conditions the main Cu species is hydroxyl ion (OH^-). They further reported a dominance of different Cu species at different soil pH values. This shows that the solubility of Cu in soils depends on the type of its chemical species present in soils as well as the quantities of either humic or fulvic acid present. In the present study, Cu solubility was enhanced at pH 5.5 to 6.5. However, the experimental set up in the present study did not include determination of the type of Cu species in the leachate water.

4.3 Influence of Cow Manure and Soil pH on Cu Solubility in Mwanga Soils

Organic matter did not have a significant effect on Cu solubility between organic matter treated soils and control soils [40]. This phenomenon corresponds with that for MW soils in the present study (Table 3). This testifies that Cu solubility is influenced by a number of factors such as the pH of leaching water, buffering capacity of soils, organic matter amendments in the soil, soil types, the formation of Cu-organic complexes, the total Cu load and the joint effects of these factors. It is probable that the manure did not influence Cu solubility in this soil type; this is in contrast with what was observed in MS soils probably due to lower total Cu load and lower levels of organic carbon in soils collected at MW than is the case for soils collected at MS.

At low soil pH, the solubility of Cu compounds was enhanced and the desorption of adsorbed Cu is consequently increased due to the competition of H^+ for adsorbing sites and an increase in positive charge on the soil surface leading to greater Cu solubility potential from the soils [41]. In coherence with these reports, Cu solubility in MW soils was higher in low pH leaching water than in high pH leaching waters in CM amended treatments. This shows that a combination of low pH and CM enhanced Cu solubility in MW soils. The converse trends manifested between MW and MS amended soils can be attributed to the aging effect. MS soils had not received Cu based fungicides for more than 10 years and therefore Cu is expected to have reverted to chemical species which are less soluble under acidic conditions; whereas MW soils are still receiving Cu based fungicides. Recently added Cu in soils exists in free Cu^+ forms and this form is more soluble under acidic conditions [39].

4.4 Influence of Total Cu Load on Cu Solubility

The solubility of Cu in long term Cu contaminated soils is proportional to the total Cu load and that the free Cu ion activity, which is the main species of bioavailable Cu, increases with an increase in total Cu contents and decreases with an increase in soil pH [29]. Results in the present study fit very well with other findings [29]. A Soil collected from MS had a total Cu load of approximately 5 times fold than the soils collected from MW. Consequently, soils collected from MS exhibited a Cu solubility of up to 4 fold higher than in MW soils (Table 3).

5. CONCLUSSION

The soils under the study were well buffered and they resisted wide variation in pH and therefore the effects associated with the lowering of soil pH as a result of acid rains or that of raised soil pH as a result of over liming may not manifest. The interaction effects of total Cu load, pH and cattle manure significantly affected Cu solubility in the two soils differently.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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