Immobilization of Copper and Fluoride in Soils: Uptake by Chinese Cabbage

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Abstract

Elevated concentrations of fluoride (F) and copper (Cu) in food substances cause health problems. Effects of Wood ash, Cattle manure and CAN+NPK on mobility and uptake of Cu and F by Chinese cabbage were explored. The soils in this study were collected from Arusha, Tanzania. The experiment was completely randomized design with four treatments, each replicated four times. Four Chinese cabbage seeds were sown in the sieved soil samples (1 kg) and sown in 1 L containers. The Chinese cabbage were irrigated daily and allowed to grow for six weeks, and harvested. Organic amendments decreased the soluble fractions of Cu and F in the soils and reduced their uptake by Chinese cabbage. For fluoride, although significant reductions were observed, the concentrations were still above the allowed concentrations for human consumption. The Wood ash treatment was generally the most effective treatment of all. It was revealed that $\log_{10}$ of Cu concentrations in Chinese cabbage was positively related with $\log_{10}$ concentration of F in the plants, elucidating that the presence of one contaminant will generally enhance the uptake of the other. It was concluded that the amendments reduced the possibility of contaminating the food chain by the two pollutants in the soils.

Keywords: uptake, amendment, organic, inorganic, contamination

Introduction

Pollution in agricultural soils has negative effects on productivity (Godson-ibeji and Chikaire, 2016) and poses negative effects to public health. Some of these pollutants, especially heavy metals are non-biodegradable; they therefore persist in the environment and therefore they pose long-term negative health effects to living organisms. For example, the uptake of F and Cu by humans has been associated with several health problems including fluorosis (Fordyce et al., 2007) and increased risk of hypertension (Bergomi et al., 1997), respectively.

In Arusha, Tanzania, majority of the people experience dental and skeletal fluorosis (Kaseva, 2006) because of the prolonged uptake of water with elevated quantities of fluoride. Apart from the uptake of fluoride through water, fluoride uptake through food substances contaminated with F can add to the total F uptake by humans. Thus, F content in food should be given due weight in assessing the total F uptake (Bhattacharya et al., 2017). Research information shows that the plant availability of F is inconsistent, with reports on high mobility, medium mobility, and immobility. This shows that F bioavailability is soil and or plant specific.

In Northern regions of Tanzania, F toxicity signs in human beings are ubiquitous. In Arusha, the levels of dental fluorosis observed is a result of uptake from water and food (Kaseva, 2006). According to (Kaseva, 2006), other food additives such as trona, which contain elevated quantities of F, may contribute to F intake by humans. Information on the contribution of drinking water on F toxicity to human beings is available; however, information on the F intake through food is scant in literature. Furthermore, much research has been carried-out on methods of removing F from the drinking water (Baunthiyal and Ranghar, 2015). Ways to immobilize F in soils and reduce its bioavailability to plants is inadequate (Baunthiyal and Ranghar, 2015).

Arusha region especially in the coffee growing areas face a problem of copper toxicity as a result of heavy and longtime use of copper based fungicides in controlling fungal diseases (Senkondo et al., 2015). Other sources of Cu in soils, in general include irrigation water (Omron and Nadeem, 2012). Scholars (Li et al., 2019) reported positive relationship between soluble F contents in the soils and total Cu load; and that Cu and F contents in maize and wheat roots increased with increased Cu contents in the soils. Very little is reported on the effects of multiple pollutions on the uptake by crops to ascertain whether the two pollutants are antagonistic or synergetic. The information will provide means of reducing the transfer of contaminants into the food chain. This will increase our understanding on the consequences of the occurrence of multiple contaminants on the uptake of both contaminants and to explore possibilities of immobilizing them in the soils in order to hinder their plant uptake.

Materials and Methods

2.1 Description of the study area

Soil samples used in this study were taken from Maji ya Chai Ward, Arumeru District in Arusha region, Tanzania. Arusha is well known for its high quantities of F in water and in soils; as a result, there has been a prevalence of dental fluorosis in the area. Coffee farms in the area have been treated with fungicides with copper as part of active ingredient to control fungal diseases and therefore elevated quantities of Cu have been encountered in coffee farms.

One soil sample was collected at 0 – 20 cm from a maize farm that had never received copper-based fungicides and two samples were collected from farms that received copper-based fungicides for a long time. The collected soil samples were taken to Ardhi University Environmental Science Laboratory for analysis and for green house experiments. The collected soil samples were dried for five days. The dried samples were passed through a 2 mm sieve after grinding.

2.2 Experimental design

The experimental design was a completely randomized with four replicates each. The soils described under 2.1 were treated with different amendments. These are; Cattle manure (60 g kg^{-1}), wood ash (10 g kg^{-1}) and NPK+CAN fertilizers. The treatments and descriptions are presented in Table 1. This experiment was carried-out in a greenhouse. About 4 Chinese cabbage seeds were sown in the sieved soil samples (1 kg) and put in 1 L containers. The vegetables were irrigated daily, allowed to grow for six weeks, and harvested.

Table 1. *Experimental treatments and description of soil categories*

Treatment No.	Treatment	Description of soil types	
		Soil type	Description
1	Soil type A - No amendment added	A	High Cu and F contents
2	Soil type A + 60g Cattle manure		
3	Soil type A + 10g Ash		
4	Soil type A + NPK +CAN		
5	Soil type B - No amendment added	B	Moderate Cu and High F contents
6	Soil type B + 60g Cattle manure		
7	Soil type B + 10g Ash		
8	Soil type B + NPK +CAN		
9	Soil type C - No amendment added	C	Background Cu and high F concentrations
10	Soil type C + 60g Cattle manure		
11	Soil type C + 10g Ash		
12	Soil type C + NPK +CAN		

2.3 Soil analysis

Soil pH was determined at 1:2.5 soil water ratio using HACH Sension, 378 with model sensors, 5191000. The 1:2.5 soil water ratio solution was used to determine Electrical conductivity (EC) using EC HACH Sension, 378 with model sensors, 51935-00-CND. The water and soil were shaken for two hours in a mechanical shaker and the pH and EC determined (ISRIC 2002.). Copper was extracted using two extractants, 0.01 M $CaCl_2$, which represents a soluble fraction and *aqua-regia*, which represents the total content (Houba et al., 2000). The Cu contents were determined using flame atomic absorption spectrometer (Analyst 100, PerkinElmer Bodenseewerk, Germany).

Total fluoride concentrations in the soil was measured (Ruan et al., 2003). In this method, 0.5 g of oven dried soil at 105^0C was taken in 50 mL beaker; and 25mL of NaOH solution was added (4.5 g of NaOH), and left for 2 hours to dissolve then stirred after 30 minutes followed by filtering. The solution was made to 50 mL mark with 2 M NaOH solution in a conical flask. About 25 mL of the solution were taken into a beaker and the total ion strength adjusting buffer (TISAB) was added followed by the determination of fluoride using a fluoride ion selective

electrodes. Water soluble F was determined; 20 g of oven dried soil samples were taken into 50 mL beakers, and 20 mL of distilled water were added and left overnight. The suspension was filtered in a 50 mL volumetric flask and made to the volume with distilled water. Twenty five millilitre (25 mL) of the aliquot were transferred into a 50 mL beakers and the total ion strength buffer (TISAB) was added and F was analyzed using fluoride ion selective electrodes (Model 51928 Platinum series).

The analysis of water extractable fluoride was established by mixing 20 mL of de-ionized water with 20 g of pulverized and sieved through 2-mm nylon sieve soil sample in 100 mL beaker. The mixture was stirred and left to settle overnight, then filtered on whatman no. 42 filter paper in a 50 mL volumetric flask and then distilled water was added to 50 mL mark. Twenty five (25 mL) of the aliquot was mixed with TISAB and stirred. Fluoride content was measured using ion specific electrodes (Model 51928 Platinum series).

2.4 Analysis of plant materials

The determination of copper in plant materials was carried-out as follows: The harvested Chinese cabbage plants were air dried for eight days then oven dried at 70 ^{o}C. The dried and ground plant materials were passed through a 1 mm sieve. The sieved plant materials were mixed with concentrated Nitric Acid and heated at 150 ^{o}C for two hours. Hydrogen peroxide was added successively after every 30 minutes until a total of 4 mL was attained. The solutions were left to cool then filtered in 25 mL volumetric flasks. The solutions were made to the mark using 2 M HNO_3. The Cu contents were measured by AAS.

Fluoride in plant materials was determined (Yadav et al., 2012); 0.5 g of oven dried, grounded and sieved Chinese cabbage samples were put into 50 mL centrifuge tubes, and 25 mL of Conc. Nitric Acid were added then left overnight. The tubes were put in the water bath (80^{O}C) for four hours. The tubes were cooled then filtered on 0.45 µm filter membrane. Distilled water was used to fill up to 50 mL with distilled water in conical flasks. Then, 25 mL were taken into a 50 mL beakers and the total ion strength buffer was added and analyzed using fluoride ion selective electrodes.

Results and discussion

3.1 Effects of amendments on soil pH

Soils used in the study were all in the acidic range with low to high Cu contents and all had elevated quantities of F (Table 2).

Table 2. *Properties of soil types used in the experiment*

Soil Sample	pH	OC (%)	EC (µs/cm)	CEC (cmol kg^{-1})	Total Cu (mg kg^{-1})	Total F (mg kg^{-1})
Sample 1	6.1	1.30	1660	79.58	735	24312
Sample 2	5.18	1.03	2320	67.70	215	17521
Sample 3	6.12	1.49	1390	28.38	37	22820

In the present study, cattle manure, wood ash, and the NPK + CAN fertilizers (p=0.05) increased significantly the soil pH of all the three soil types as compared with the control treatments (treatments with no amendment addition) as detailed in Table 3.

For soil type 1, wood ash treated soils had the highest increased pH than the other amendments. There was no significant difference in pH alteration between Cattle manure and NPK + CAN amended treatments. For soil type 2, NPK + CAN treatment did not significantly increase the soil pH in comparison with the control treatment whereas Cattle manure and Wood ash significantly enhanced the pH in comparison with the control treatment. The effect of the amendments, Cattle manure and the Wood ash on pH changes was insignificant. For soil type 3, all the three amendments had significantly increased the soil pH in comparison with the control treatment. However, the effects on soil pH among the amendments were insignificant. Soil pH is the main driver of solubility of metals in soils (Najafi and Jalali, 2016) because it is the main determinant of metal and Fluoride speciation and mobility (Kumpiene et al., 2006). In all the three soil types, the Wood ash treatment had consistently the highest pH among the three amendments. This treatment (Wood ash) had the lowest Cu (see sections, 3.2 to 3.5). This shows that Wood ash is the most effective F and Cu immobilizer compared to the other amendments used due to its liming effect that raises the pH of an acidic or neutral soil. The liming effect is attributed to the presence of oxides, hydroxides, carbonates, and silicates containing calcium and other bases (Harden and Pitt, 2013).

Table 3. Variations of soil pH under different treatments

Treatment/ Parameter	Mean Soil pH (n=4)		
	Soil type 1	Soil type 2	Soil type 3
No amendment added	6.1^{c}	5.2^{b}	6.1^{b}
Soil + 60g Cattle manure	8.4^{b}	8.4^{a}	8.9^{a}
Soil + 10g Ash	10.4^{a}	8.9^{a}	9.6^{a}
Soil + NPK +CAN	7.9^{b}	6.69^{b}	8.2^{a}

The same letter in the same column are not statistically different according to Tukey's method (p=0.05)
The same number in the same row are not statistically significant (p=0.05)

3.2 Effects of amendments on F solubility

For soil type 1, results show that all the three amendments significantly (p=0.05) reduced the solubility of F (Table 4).

Table 4. *Soluble F contents (mg kg^{-1})*

Treatment/ Parameter	Mean Soil Soluble F (n=4) (mg kg^{-1})		
	Soil type 1	Soil type 2	Soil type 3
No amendment added	161^{a2}	93^{a3}	216^{a1}
Soil + 60g Cattle manure	94^{b1}	70^{a1}	81^{b1}
Soil + 10g Ash	71^{b1}	26^{b3}	63^{bc2}
Soil + NPK +CAN	49^{bc2}	$75^{a1,2}$	103^{c1}

The same letter in the same column are not statistically different according to Tukey's method (p=0.05)
The same number in the same row are not statistically significant (p=0.05)

The most reduced treatment for the soil type was NPK + CAN, followed by Wood ash and the Cattle manure was the least. The reduction in F solubility between the cattle manure and the wood ash treatments were not significant. For soil type 2, only wood ash amended soils significantly reduced the solubility of F and this can be a result of the elevated soil pH associated with the addition of the ash (Wambu et al., 2016). The F solubility for soil type 3 was reduced in all the treatments with the most reduced F concentration being the Wood ash treatment and then the Cattle manure, while the NPK + CAN treatment was the least reduced. The increased pH in the present study resulting from the addition of different amendments corresponded with the decreased F solubility (see Figure 1). Upon degradation, organic matter amendments produce negatively charged functional groups on their surface, for example –OH,–COOH, and–NH_2), which can be replaced by F− (Chen et al., 2010), thereby making the F^- immobile in soils.

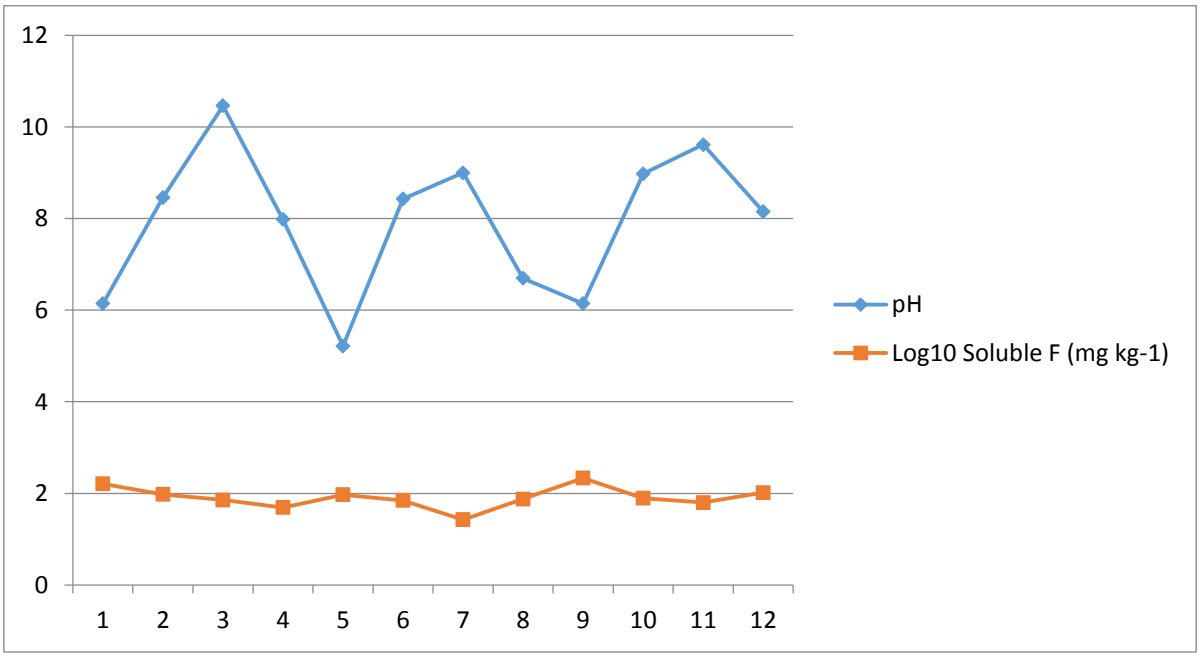


Figure 1. *Relationship between soil pH and solubility of F (mg kg^{-1}) in soils*

The reduced soluble F contents in the soil solution due to addition of the amendments implies that F–root contact has been significantly reduced. This is a very important process in detoxifying the soils because the water soluble F fraction is the one that is in contact with the biological system and is the one that is bioavailable. The bioavailable F fraction indeed poses a threat of contaminating the food web. Since these inorganic amendments contain essential elements for plants nutrition, it is quiet practical to use the materials as plant nutrients as well as F decontamination materials.

It is imperative therefore to integrate the inorganic fertilizers in soil fertility as well as in the environmental sanitation programs thereby offering a production system that would reduce excessive uptake of F. Further research therefore should be geared towards investigating the right rate of the fertilizer materials that are optimum for crop production and that would

immobilize F to the levels that can reduce F uptake to acceptable levels. Since cattle manure also showed F immobilization potential, it is plausible to carry-out further experiments that would combine cattle manure and inorganic fertilizers to explore the possible synergy of the combined effects of the two types of amendments on F and Cu immobilization. It is also prudent to carry-out further studies on the long-term effects of these amendments on soil health and crop safety.

Table 5. *$CaCl_2$ extractable Cu (mg kg^{-1})*

Treatment/ Parameter	Mean soluble ($CaCl_2$) extractable Cu (n=4)		
	Soil type 1 (High Cu content)	Soil type 2 (Moderate Cu content)	Soil type 3 (normal Cu content)
No amendment added	4.8^{a1}	2.6^{a2}	1.6^{a2}
Soil + 60g Cattle manure	2.3^{b1}	$1.4^{b1,2}$	0.9^{ab2}
Soil + 10g Ash	1.1^{c1}	0.5^{b1}	0.4^{b1}
Soil + NPK +CAN	1.7^{b1}	$0.9^{b1,2}$	0.7^{b2}

The same letter in the same column are not statistically different according to Tukey's method (p=0.05)
The same number in the same row are not statistically significant (p=0.05)

3.3 Effects of the amendments on Cu solubility

For soil type 1 and 2, Cattle manure, Wood ash and the inorganic fertilizers significantly (p=0.05) reduced the $CaCl_2$-extractable Cu (Table 5) compared with the control treatments. For soil type 1, the wood ash treatment was the most immobilized one, whereas the Cu immobilization between NPK + CAN and Cattle manure treatments were not significantly different.

The concentration of $CaCl_2$-extractable Cu between control and the Cattle manure amended soils did not differ significantly for soil type 3. But the concentration of $CaCl_2$-extractable Cu for Wood ash or NPK +CAN amended soils was significantly lower than the control soils. However, the $CaCl_2$-extractable Cu among the three amendments in the three soil types was not significantly different except for the Wood ash treatment which had the lowest $CaCl_2$-extractable Cu concentration and therefore the wood ash was the most effective amendment in reducing Cu solubility as compared with the other amendments.

The increased soil pH (Table 3) observed resulting from the addition of the amendments matched with the decreased water soluble $CaCl_2$-extractable Cu (see Figure 2). Increased pH as a result of addition of the amendments may lead to Cu^{2+} hydrolysis forming $Cu(OH)^{+}$ and precipitating Cu as hydroxides ($Cu(OH)_2$) thereby making it insoluble and less bioavailable (Sebastia et al., 2007). The reduction in the metal solubility under elevated soil pH conditions can also be explained by increased adsorption capacity of the soils due to enhanced negative charges on soil colloids under alkaline conditions (Soltan and Ismail, 2019).

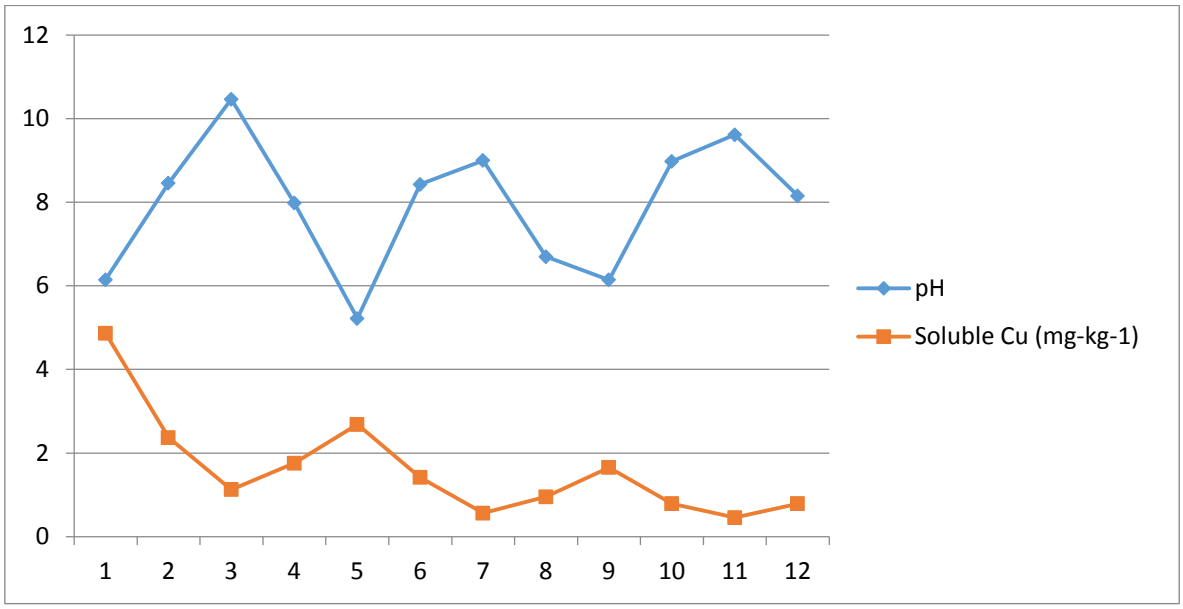


Figure 2. *Relationship between $CaCl_2$ extractable Cu and soil pH*

Elevated Copper contents in the soils (Table 2) were due to long-term use of copper-based fungicides. The farm that had background copper concentrations had never received copper containing fungicides. Continued use of fungicides therefore was the cause of the elevated Cu quantities observed. The soluble Cu contents encountered were very low (Table 5) as compared to the total Cu contents (see Table 2). Cu forms stable complexes with organic matter (Rieuwerts, 2007) and forms inner-sphere complexation culminating in its immobilization in the soils (Karlsson et al., 2006). For the un-amended treatments, it was found that soils with the highest total Cu load (Table 1) had higher soluble Cu than the moderately Cu contaminated soils and the soils with the background Cu concentrations (Table 5). Although soil pH is the major driver of Cu solubility in the soils (Najafi and Jalali, 2016), the pH values among the three soil types were not significantly different at p=0.05 (Table 3). Therefore, the higher concentrations of $CaCl_2$ extractable copper encountered in the soil can be attributed to the higher total Cu load in the soils due to use of copper-containing fungicides for a long time.
Inorganic fertilizers used in the present study contained Nitrogen, Phosphorus and Potassium (NPK), and Calcium Ammonium Nitrate (CAN). Phosphates are one of the decomposition products of organic matter, which can immobilize Cu in the soils. Cu may form stable complexes with humic substances, thereby reducing the solubility of Cu especially when high molecular weight compounds are formed (Liu et al., 2009) because Cu has strong affinity to specific sites of the organic matter molecules that lead to formation of stable complexes.

3.4 F Concentrations in plants

The concentration of F in Chinese cabbage plants encountered in the present study varied from 221 mg kg^{-1} to 3607 mg kg^{-1} (Table 6). There was a significant reduction in F uptake by Chinese cabbage as a result of addition of all the three amendments. For soil type 1, wood ash treatment had significantly lower F concentrations than the other two treatments

(p=0.05) whereas the concentrations of F between Cattle manure and NPK+CAN were not significantly different. For soil type 3, the amendment that showed the highest reduced uptake of F was Wood ash, followed by NPK + CAN and the Cattle Manure was the least. In all the three soil types, Wood ash was the most effective F immobilizing treatment and the reduced uptake can be a result of liming effect of the Wood ash.

Table 6. *Concentrations of F in plants (mg kg^{-1})*

Treatment/ Parameter	Mean F in plants (n=4) (mg kg^{-1})		
	Soil type 1	Soil type 2	Soil type 3
No amendment added	1756a^{2}	1010^{a3}	3607^{a1}
Soil + 60g Cattle manure	697^{b1}	607^{ab1}	1561^{b1}
Soil + 10g Ash	363^{b1}	221^{b1}	524^{d1}
Soil + NPK +CAN	610^{b1}	552^{b1}	856^{c1}

The same letter in the same column are not statistically different according to Tukey's method (p=0.05)
The same number in the same row are not statistically significant (p=0.05)

The F concentration in Chinese cabbage observed was well above the normal F contents reported for several crops worldwide. The amendments added to the soils apart from reducing the soluble F contents in the soils (Table 4), deterred F uptake by Chinese cabbage by up to 6 fold. Wood ash and NPK + CAN treatments showed higher reduction in F uptake than the Cattle manure treated soils. This can be attributed to the presence of Calcium in the two amendments which have a liming effect that increased soil pH. Furthermore, Calcium containing compounds precipitate F in form of CaF_2 (Álvarez-Ayuso et al., 2011) in soils and reduce its availability to crops (Baunthiyal and Ranghar, 2015). Another mechanism of reduced F uptake by plants has been postulated (Ruan et al., 2004). They argue that calcium reduces cell membranes permeability of plants to Fluoride. That Calcium is an important constituent of plant cell walls and membranes and therefore its presence in cell walls reduces F uptake by plants due to reduced passage of F. Apart from precipitating F in the soils, Ca, which is present in plant cell walls acts as a buffer against F accumulation (Baunthiyal and Ranghar, 2015). The highest F concentrations in Chinese cabbage corresponded with the treatment with the highest concentrations of water soluble F (Tables 4 and 6) elucidating that the total F load determines the quantities of F to be taken by the Chinese cabbage.

3.5 Copper concentrations in plants

Amendments added to soils apart from decreasing the $CaCl_2$ extractable Cu, they as well significantly (p=0.05) deceased the uptake of Cu by the Chinese cabbage (Table 7). For soil type 1, the treatment that immobilized the Cu most was Wood ash followed by NPK + CAN and the Cattle manure was the least. In general, for soil type 1, the amendments immobilized the Cu by 9.2 fold (Wood ash), 7.1 (NPK + CAN) and 3.7 (Cattle manure). For soil type 2 and 3, a similar trend was observed but with different magnitudes of immobilization. For example, for soil type 2, Wood ash immobilized Cu by 9.5 fold (wood ash), by 3 fold (NPK + CAN) and 2.3 fold (Cattle manure). Whereas for soil type 3, wood ash immobilized Cu by 9 fold, NPK + CAN reduced Cu uptake by 3.8 fold and the cattle manure

reduced Cu by 3 fold. The rate of immobilization by Wood ash was relatively the same for all the soil types, making it the most effective Cu immobilizer of the three amendments.

Table 7. *Concentrations of Cu in plants(mg kg^{-1})*

Treatment/ Parameter	Mean Cu in plants (n=4) (mg kg^{-1})		
	Soil type 1	Soil type 2	Soil type 3
No amendment added	34.1^{a1}	17.1^{a2}	13.5^{a2}
Soil + 60g Cattle manure	9.1^{b1}	7.4^{b1}	4.5^{b1}
Soil + 10g Ash	3.7^{c1}	1.8^{c1}	1.5^{b1}
Soil + NPK +CAN	4.8^{bc1}	5.8^{bc1}	3.6^{b1}

The same letter in the same column are not statistically different according to Tukey's method (p=0.05)
The same number in the same row are not statistically significant (p=0.05)

The highest mean Cu concentration observed in this study was 34 mg kg^{-1} and this happened in the soils with the highest concentrations of Cu without any amendments added. Several authors reported different critical levels of Cu in the plants above which toxicity is observed. The reported deficiency levels of Cu in plants ranges from 1 and 2 mg kg^{-1} and Cu toxicity was reported for concentrations in the plants above 20 mg kg^{-1} (Kabata-Pendias and Pendias, 2001). Therefore all the amended treatments had Cu concentrations well below the critical Cu concentrations in healthy plants.

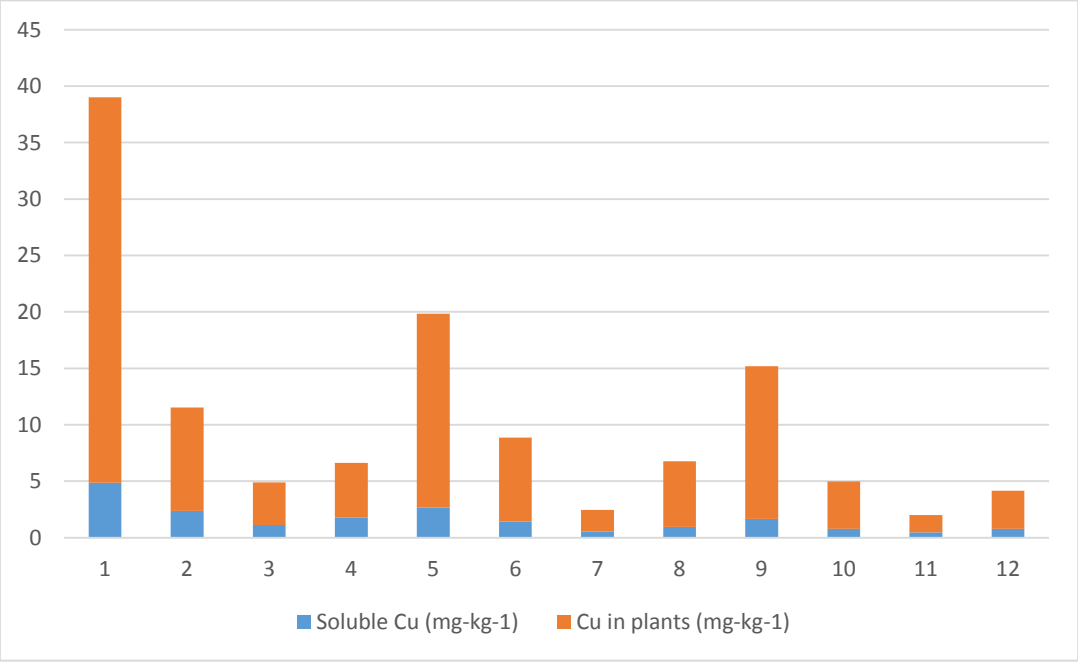


Figure 3. *Relationship between $CaCl_2$ extractable Cu and Cu concentrations in Chinese cabbage plants*

The contents of Cu observed in this study for the soils, which were highly contaminated surpassed the concentrations of Cu for normal plants. A decrease in Cu concentrations in Chinese cabbage plants grown on amended soils corresponded with a decrease in the contents

of $CaCl_2$ extractable Cu. For example, the highly Cu contaminated soils (Figure 3) had the highest $CaCl_2$ extractable Cu contents and the highest concentrations of Cu in Chinese cabbage plants and vice versa. This shows that the amendments effectively reduced the uptake of Cu below toxic levels.

It is important to include these amendments in plant management programmes as fertilizer materials as well as detoxification materials. Importantly, further research should be carried to establish optimal levels that will ensure optimum reduction of Cu uptake as well as ensuring optimum nutritional and production requirements.

3.6 Relationship between concentration of F and Cu in soils and in plants

It was found that Cu concentrations in Chinese cabbage increased with an increase in log_{10} of soluble F in the soils (Figure 4), elucidating that F and Cu have a positive relationship. This relationship shows that the presence of one of the contaminants in soils enhances the uptake of the other thereby increasing a risk of contaminating the food web.

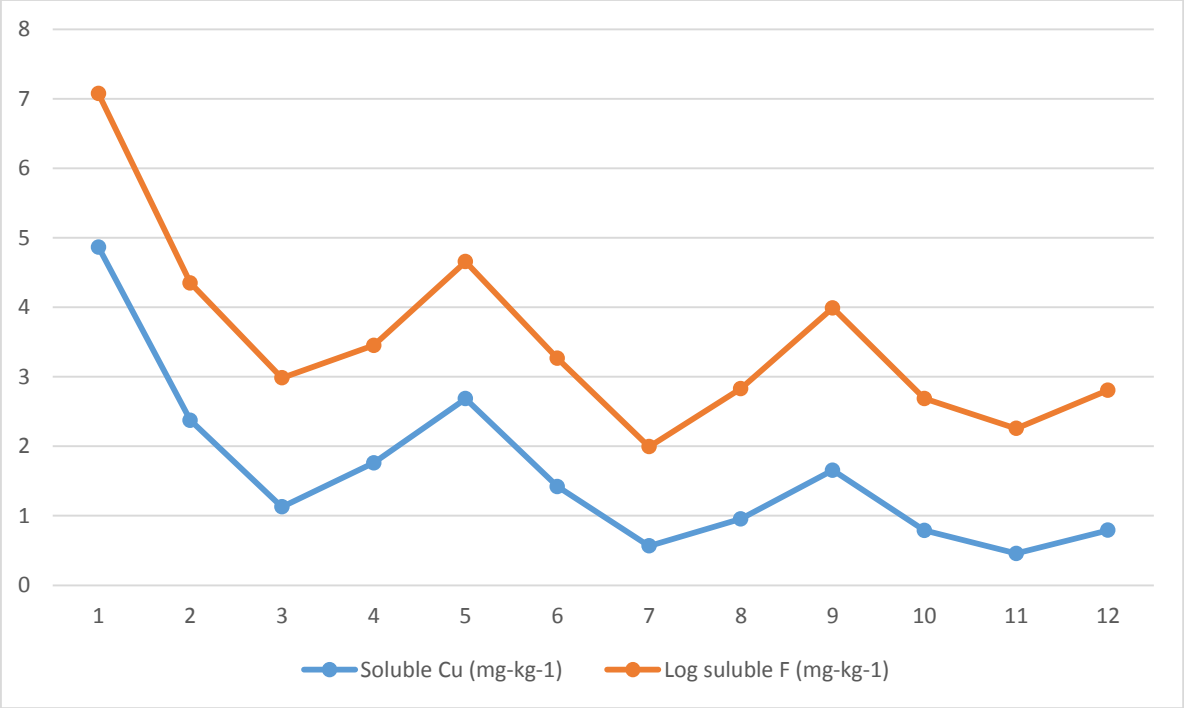


Figure 4. *Relationship between Soluble Cu (mg kg^{-1})and soluble F (mg kg^{-1})*

In the present study, it has been observed that the solubility and uptake of Cu or F is a function of the total Cu or F load in the soils. This means that with increased levels of either F or Cu contamination, the higher the uptake of the either pollutant, leading to elevated risks of polluting the food web (Figure 5).

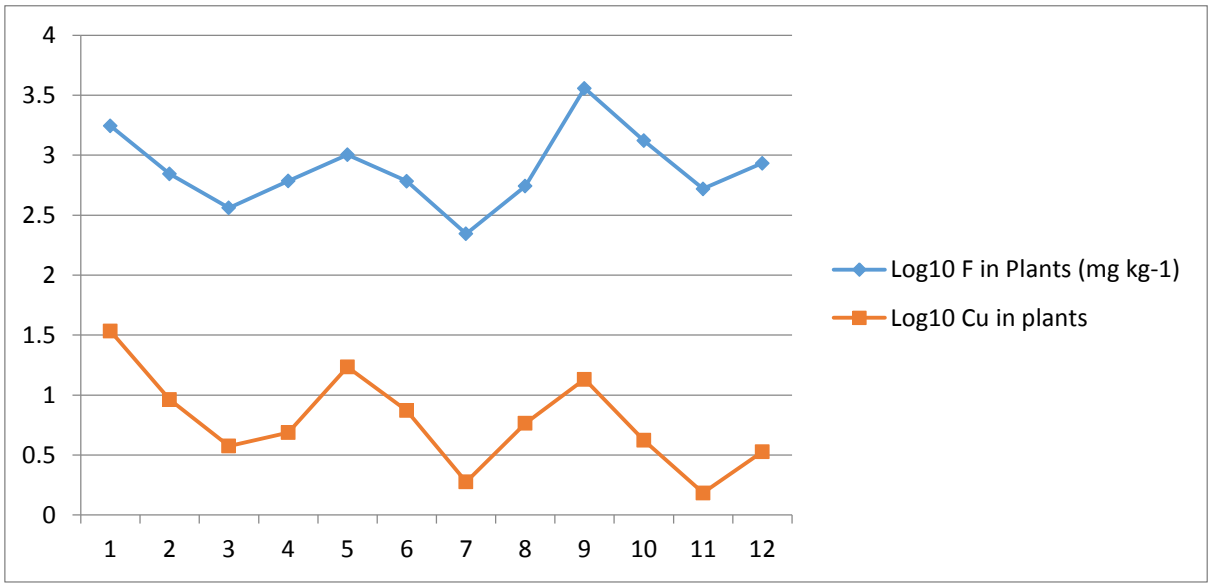


Figure 5. *Relationship between F concentrations in Chinese cabbage plants (mg kg^{-1}) and the concentrations of Cu (mg kg^{-1})*

Studies have revealed that the total Cu contents in the soils have a positive relationship with water soluble F and that Cu enhanced the solubility and accumulation of F in wheat leaves (Li et al., 2019). Furthermore, the authors reported that water soluble F fractions of some soils was positively related to the exchangeable fractions of Cu, showing that the soluble fractions of F can retain Cu in exchangeable fractions. The relationship between the soluble fractions of F and Cu in the soils can be attributed to the fact that F can form complexes with Cu (Cu-F complexes) and stay in a stable condition in aqueous solution (Manivannan et al., 2008). Very few literatures have explored the relationship between Cu and F in soils and in plants. It is important therefore to perform further studies in order to increase the understanding of the dynamics of these two pollutants in agricultural soils.

Conclusions

In conclusion, the organic amendments increased soil pH, and decreased the concentrations of Cu and F in the soils and consequently reduced their uptake by Chinese cabbage plants. Therefore, these amendments can reduce the possibility of contaminating the food chain as a result of the presence of the two pollutants in the soils. Although the amendments deterred the uptake of Cu and F by Chinese cabbage, the quantities of F encountered were well above the normal F contents in normal plants. Therefore, these soils should not be used to grow Chinese cabbage. However, the amendments successfully deterred the uptake of Cu by Chinese cabbage, and therefore the Cu concentrations did not surpass the normal F contents. Therefore, Cu in the amended soils does not pose a risk of polluting the food web.

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