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Copper in water-soil-plant interactions: food chain toxicity due to irrigation with Asa River in Ilorin, Nigeria

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ABSTRACT

Asa River is the most important river that serves as a cheaper and easier disposal alternative to industries and at the same time as a less expensive and dependable water supply to farmers for the production of vegetables in dry season in Ilorin, the capital city of Kwara State, Nigeria. To investigate the effect of Asa River water pollution on water-soil-plant copper (Cu) mobility, a two factor factorial in randomized complete block design (RCBD) survey was conducted. The factors comprised of Factor A: distance between irrigation water sources and Factor B: irrigation history (irrigation duration in years). Four (4) farming locations, which corresponded to a control location 200 m upstream (– 200 m location), 200, 400 and 600 m downstream were selected. At each location, 4 farmers with different irrigation history were selected and the study was replicated thrice. The irrigation history was 0, 10, 20 and 30 years of irrigation with Asa river water. The results indicated that Cu levels in Asa River obtained 600 m downstream of control location, exceeded permissible limits with levels as high as 4.51 mg/L. Soil and plant tissue Cu concentrations were also found to exceed permissible levels, with plant tissue Cu reaching as high as 81.86 mg/kg in *Corchorus olitorius*.

Introduction

Water is vital to the existence of all living organisms, but this valued resource is being threatened increasingly as human population grows and demands more water of a high quality for domestic purposes and economic activities (UNEP, 2000). The quality of any body of surface or ground water is a function of either or both, natural influences and human activities (Stark et al., 2001; Kolawole et al., 2008). Water is also a vital resource for agriculture, manufacturing, transportation and many other human activities. In agriculture, especially dry season vegetable production, water sources other than rainfall, which may for instance include streams, rivers, dams and ponds, are of paramount importance. Despite its importance, water is

the most poorly managed resource in the world (Ajadi, 2016). Rivers are the most important freshwater resources for people. Unfortunately, rivers are being polluted by indiscriminate disposal of sewage, industrial waste and a plethora of human activities, which affect their physico-chemical characteristics and microbiological quality (Koshy and Nayar, 1999). Heavy metals are one of the river pollutants in urban and semi urban areas. Heavy metals that have been identified in the polluted environment include As, Cu, Cd, Pb, Cr, Ni, Hg and Zn. The presence of any metal may vary from site to site, depending upon the source of an individual pollutant. Plants take up heavy metals by absorbing them from deposits on the parts of the plants exposed to the air and/or from contaminated soils (Kachenko and Singh, 2006). Excessive uptake of heavy metals by plants may produce toxicity in human nutrition, and cause acute

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and chronic diseases. For instance, Cu is an essential micronutrient required in the growth of both plants and animals. In humans, it helps in the production of blood haemoglobin. In plants, Cu is especially important in seed production, disease resistance, and regulation of water. Copper is indeed essential, but in high doses it can cause anaemia, liver and kidney damage, stomach and intestinal irritation (Eriksson, 1997). Copper normally occurs in drinking water from Cu pipes, as well as from additives designed to control algae growth. Plant species have a variety of capacities in removing and accumulating heavy metals. So there are reports indicating that some plant species may accumulate specific heavy metals (Markert, 1993). The uptake of metals from the soil depends on different factors, such as their soluble content, soil pH, plant species, fertilizers, and soil type (Lübben and Sauerberck, 1991). Water supply is a route through which some of these metals are introduced into soils and plants.

Asa river supplies the bulk of water used by people in Ilorin and it's suitable for different activities. Some use it for laundry washing and recreation, for some industries it supplies cooling water, and to others it is a convenient point of waste discharge from both home and industries (Adekola and Eletta, 2006). It is however dammed at some point, treated and distributed to serve the domestic needs of people (Eletta et al., 2006). The objective of this study was to determine how safe Asa river is for irrigation purposes in terms of its Cu content.

Materials and Methods

Description of experimental location

Ilorin is the capital of Kwara State. It is located at $8°35'$ E latitude and $4°35'$ N longitude (Jimoh, 2011), with a total land area of about 100 km² (Kwara State Government, 2007). The climate of Ilorin is the humid tropic type and characterized by both wet and dry seasons with mean annual temperature that ranges from 25-28.9 ℃ and the annual mean rainfall is about 1150 mm. During the dry season from November to February, days are very hot and nights are cool. Temperature typically ranges from 33-34 ℃, while from February to April, values are frequently between 34.6 and 37 ℃. Ilorin is located in the transition zone between the deciduous forest (rainforest) on the southwest and the savannah grasslands on the north (Oyegun, 1982). The vegetation of Ilorin is composed of species of plants such as locust bean trees (*Parkia biglobosa)*, shear butter trees (*Vitellaria paradoxa*), acacia trees (*Acacia spp*.), baobab trees (*Adasonia digita*), elephant grasses (*Pennisetum purpereum*),

shrubs and herbaceous plants among others (Jimoh, 2011). Jimoh (2011) also reported that basement complex rocks which are mainly composed of metamorphic rocks, especially gneiss and resistant quartzite, underlay Ilorin city. The soil of Ilorin belong to the soil group called "Ferruginous soil" which are reddish-brown in colour and has some proportion of clay content and it is formed from the precambrian basement complex rocks and it is under the grassland savannah forest cover. The dominant clay type is the kaolinite clay and illite group. The study area covered selected portions along the bank of Asa River where vegetables are cultivated with the river as source of irrigated water. The river is located in Ilorin West Local Government Area (L.G.A) and is the main river in Ilorin, flowing in a South-North direction. It divides Ilorin into two parts: a western part representing the core or indigenous area, and the eastern part where the Government Reservation Area (GRA) is situated (Oyebanji, 1993). Asa River has a surface area of 302 hectares with a maximum depth of 14 m and is located approximately 4 km south of Ilorin Township (Adekeye, 2004). The river lies between latitude $8°28'$ and $8°52'N$ and longitude $4°35'$ and $4°45'E$. The tributaries of Asa River are Agba, Aluko, Atikeke, Mitile, Odota, Okun, and Osere Rivers.

Design and layout of the survey

The survey, which was carried out in late rainy season of 2014, was of a two factor factorial in randomized complete block design (RCBD). The factors comprised Factor A: distance between irrigation water sources and Factor B: irrigation history (irrigation duration in years). Four (4) farming locations corresponded to 200 m upstream (control), and 200, 400 and 600 m downstream. At each location 4 farmers with different irrigation history were selected. The irrigation history was 0, 10, 20 and 30 years of irrigation with Asa river water. Three farmers were selected for each irrigation history to serve as replicates. The selected farmers belonged to the same social class and shared similar practices [cultivated *Telfaria occidentalis*, *Amaranthus spp. and Corchorus olitorius* on ridges, applied NPK (15:15:15), manual weeding and sprinkler irrigation]. Information on the irrigation history and farming practices were obtained by interviewing the farmers and local residents. A total of $4 \times 4 \times 3$ (48) plots of size 3.5 m² (7.0 m × 0.5 m) on ridges of dimension 15 m by 1.0 m with furrows measuring 0.5 m were sampled. The first farm site (control) was located 200 m upstream of a metal and steel works (subsequently designated – 200 m location), with coordinates N 08º 27'05.5'' E 004º 35'33.6''. The second farm location (200 m downstream) was situated

behind the metal and steel works with coordinates N 08° 28'03.1'', E 004º 33'29.7'', while the third farm (400 m downstream) was situated behind two major soft drink bottling industries (after point of effluent discharge), which is also the point where Osere River (with suspended effluents discharged from a soap and pharmaceutical industry) flows into Asa River with coordinates N 08º 28' 41.8'', E 004º 33' 34.4'' and the fourth farm (600 m downstream) was situated downstream of all the previous locations, receiving effluents from domestic sources such as sewage etc. with coordinates N 08º 29' 56.6'', E 004º 34' 08.5''.

Sample collection

Water and sediment sampling procedure

Four (4) river water and sediment samples were randomly collected in plastic bottles and polyethylene bags from each farm location; 1 L of HNO3 was immediately added to the water samples to keep the metals in a solution. The sediment samples were later air-dried in the laboratory.

Soil sampling procedure

Bulk soil samples were collected with the aid of stainless steel soil auger at each farm location to a depth of 15 cm and a composite of 2 kg was bagged in polyethylene plastic bags and taken to the laboratory for analyses.

Preparation of soil, sediment and plant samples for the physical and chemical analyses

The soil and sediment samples were air dried, crushed and sieved with a 4.75 mm sieve before physical analyses, whereas 2 mm sieve was used to prepare samples for chemical analyses in the laboratory. Plant samples were washed, air dried, milled and stored in air-tight plastic containers for chemical analysis.

Soil texture

Soil textural determination was done using a hydrometer method by Bouyoucos (1936).

Copper determination in water samples

In the procedure, 50 mL of water samples was pipetted into 100 mL beakers and 10 mL nitric acid was added. The beakers were placed on a hot plate until complete digestion; 10 mL volume was then taken in order to determine the content of heavy metals using Atomic Absorption Spectrophotometer (PerkinElmer, Germany) (AAS) (Agbenin, 1995).

Copper determination in soil, sediment and plant samples

Two grams of the soil, sediment and plant samples were separately weighed into digestion flasks and treated with 10 mL of an acid mixture made up of concentrated nitric acid (HNO_3), hydrochloric acid (HCl) and sulphuric acid (H_2SO_4). The samples were mixed and heated for 30 minutes on a hot plate at 80 – 90 ºC at which they were brought to boil and a clean solution was obtained. After cooling, the solutions were filtered with Whatman No. 4 filter paper and then transferred quantitatively to a 100 mL volumetric flask with 50 mL of de-ionized water. The solutions were then preserved in a universal bottle for further analysis. All reagents were of analytical grade and the AAS was used for the determination of copper content (Sobukola et al., 2007).

Data analysis

Data collected was analysed statistically using analysis of variance (ANOVA) with Genstat 17 statistical software and significant means was separated using least significant difference (LSD).

Results and discussion

Table 1 shows the effect of distance between water sources on Cu concentration in water sampled from Asa River. It was observed that there was a significant increase for every 200 m increase in distance downstream with the highest value of 4.51 mg/L obtained in location 600 m. The increase followed the order 600 m > 400 m > 200 m > 0 m. The observation is thought to be linked to the activities of metal and steel works, soap industry, pharmaceutical company and bottling companies, and disposal of municipal waste at points between –200 and 200 m, 200 and 400 m and 400 and 600 m, respectively. Mean concentrations of Cu at the various sampling points exceeded FEPA (1991) and WHO (1984) permissible level of 0.05 mg/L for irrigation water. Ogundiran and Fawole (2014) had similarly reported that Cu values exceeded these standard reference values. The copper control value of 1.21 mg/L is suggestive of natural inputs determined by mineralogy of parent materials. At these concentrations, copper and other heavy metals which exceed the physiological demand of plants, could not only administer toxic effect in them, but could also enter the food chain and probably get biomagnified, and thus pose a potential threat to human health.

Table 2 shows that the distance between irrigation water sources affected (p < 0.05) the concentrations of

Cu in the river bed sediments, with points 400 m downstream indicating the highest value (4.32 mg/kg), whereas the control had the lowest value (1.90 mg/kg). The river bed is a reservoir for heavy metals which become soluble and mobile depending on the pH of the water.

Table 3 indicates variations in clay content in soils between water sources and irrigation history (duration). The results showed that the clay content of irrigated soils beyond 200 m downstream was higher (9.14 – 9.67%) than those before this point (6.90 – 7.81%). The results also revealed that soils irrigated for up to 10 years had higher clay content (8.65 – 9.22%) compared to the control (6.90%). Farm soils located 400 m downstream, that have been irrigated less than 20 years, had the highest content of clay of 12.08%. According to Hillier (2003), clay, which is the active part of soil, helps in absorption capacities in various applications, such as removal of heavy metals from waste water and air purification. This exchange capacity provided by active clays is as a result of the numerous exchange sites which can also immobilize soil heavy metals, thereby making them unavailable for plant root absorption. This however depends on the prevailing pH. On the other hand, high proportions of clay in soil cause low water permeability and ploughing difficulties.

Table 4 indicates that soils under irrigation with Asa River water sourced at 400 m downstream had the highest concentration of Cu, whereas soils in control location and 200 m downstream had the lowest (2.23 and 2.07%, respectively). The effect of the irrigation history on the farm soils indicated that Cu accumulation reached a significant peak value of 4.41 mg/kg in 10 years and gradually declined to the lowest value of 3.64 mg/kg in 30 years. The effect of time on the Cu concentration of soil seems to agree to some extent with the reported findings that Cu is not magnified in the body or bio-accumulated in the food chain (Wuana and Okieimen, 2011).

Table 1. Effects of distance between water source on Cu concentration (mg/L) in Asa river

Distance between water sources in metres			
-200	200	400	600
1.21	1.23	1.20	1.19
1.23	2.62	4.25	5.61
1.20	2.61	4.19	5.57
1.19	2.57	4.17	5.65
Mean **1.21**	**2.26**	**3.45**	**4.51**
LSD 0.05 0.03			

Table 2. Effects of distance between water sources on Cu concentration (mg/kg) in Asa river sediment

Distance between water sources in metres			
-200	200	400	600
1.90	1.86	1.95	1.89
1.86	3.40	5.09	3.91
1.95	3.28	5.16	3.79
1.89	3.33	5.07	3.82
Mean **1.90**	**2.97**	**4.32**	**3.35**
LSD (0.05) 0.31			

Table 3. Effects of distance between water sources and irrigation duration on clay content of soil along Asa river

Irrigation duration in years (factor B)	Distance between water sources in metres (factor A)				
	-200	200	400	600	Mean
0	6.90	6.63	7.43	6.63	**6.90**
10	7.43	7.09	11.41	9.09	**8.76**
20	6.63	7.09	12.08	11.08	**9.22**
30	6.63	10.43	7.76	9.76	**8.65**
Mean	**6.90**	**7.81**	**9.67**	**9.14**	
LSD 0.05	Factor A =	1.33	Factor B =	**1.18**	A×B = *

The results also indicated that the highest values of Cu were obtained in farm soils irrigated for 10 years in locations 400 m downstream. Worthy of note is that this location receives effluents from bottling companies, soap and pharmaceutical industries. All Cu concentration obtained in these soils exceeded WHO/FAO (2007) critical value of 0.20 mg/kg. Soils are a major sink for heavy metals released into the environment by anthropogenic activities, and unlike organic contaminants, which are oxidized to carbon (IV) oxide by microbial action, most metals do not undergo microbial or chemical degradation (Kirpichtchikova et al., 2006), and hence soil contamination may pose risks and hazards to humans through direct ingestion or through the food chain by the reduction in food quality and land tenure problems (McLauglin et al., 1999; Zarcinas et al., 2004; Ling et al., 2007).

Fig. 1 shows that the tissue concentration of Cu in *Telfaria occidentalis* plants grown in farms located downstream of the control point was higher than that of the control, with the highest value of 4.76 mg/kg observed in plants from farms 600 m downstream. No statistical difference was, however, observed between plants in locations 200 and 400 m downstream. The effect of distance between irrigation water sources on *Corchorus olitorius*, indicated that the plant tissue Cu concentration followed the trend 400 > 600 > 200 > – 200 m. The highest value was 80.24 mg/kg, whereas the lowest was 41.28 mg/kg. Furthermore, the results showed that tissue Cu concentration was significantly higher in *Amaranthus spp.* plants grown in farms downstream of the control. The highest value of tissue Cu (6.44 mg/kg) in *Amaranthus* was obtained in location 400 m, whereas the lowest value (3.44 mg/kg) was obtained in the control location. Increased plant tissue Cu obtained in location 400 m may be a reflection of its high water and sediment Cu load. Though water samples from location 400 m had a lower Cu load compared to samples from location 600 m, the higher sediment Cu load in location 400 m could have led to higher Cu load in irrigation water sourced from location 400 m, depending on the prevailing water pH. According to Eriksson (1997), the solubility of Cu is drastically increased at pH 5.5. The effect of irrigation history/duration on the vegetables planted by the farmers across the various locations, indicated that all vegetables, irrespective of species, accumulated Cu most rapidly as the irrigation history increased from 0 – 10 years compared to durations from 10 – 20 years and 20 – 30 years (Fig. 2). Farm soils with irrrigation history of 0 – 10 years, which had earlier been observed to have peak accumulation of soil Cu concentration, similarly produced vegetables with peak values of tissue Cu. Among the three vegetables covered in this survey, the rate of accumulation in tissue Cu was highest in *C. olitorius.* In the same vein, the plant's highest tissue Cu concentration (81.86 mg/kg) reached values more than ten times higher than those in *T. occidentalis* (4.76 mg/kg) and A. spp.(6.44 mg/kg) and twice higher than FAO/WHO (2001) acceptable limits of 40 mg/kg. This result raises serious concern for urgent follow-up confirmatory investigations, taking into account that *C. olitorius* form part of the daily meal of the dominant population of Ilorin city who are of the Yoruba ethnic extraction. Shuaibu et al. (2013) had earlier reported highest concentration of Cu in wild jute (*C. olitorius*) among three other vegetables surveyed in Katsina, North-western Nigeria. Kachenko and Singh (2006) reported that heavy metals are non-biodegradable and persistent environmental contaminants. Plants take up heavy metals by absorbing them from deposits on the parts of the plants exposed to the air from polluted environments as well as from contaminated soils. Nriagu (1990) also reported that heavy metal pollution of soil, water, and atmosphere represents a growing environmental problem affecting food quality and human health in cities. Copper, in high doses, has been reported to cause anaemia, liver and kidney damage, stomach and intestinal irritation (Eriksson, 1997).

Table 4. Effects of distance between water sources and irrigation duration on Cu concentration (mg/kg) in the soil

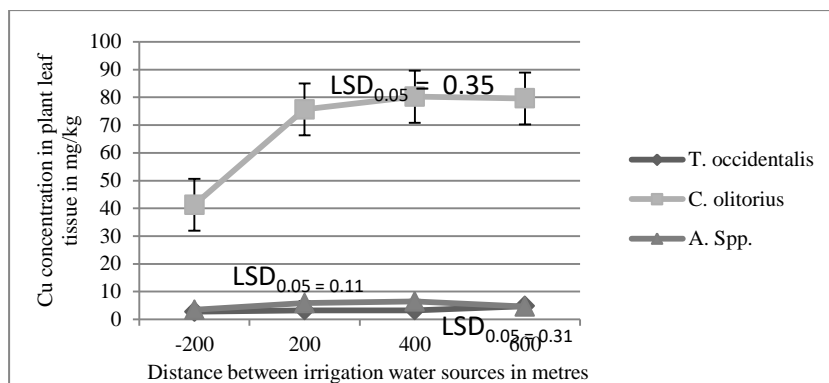| Irrigation duration in years (factor B)	Distance between water sources in metres (factor A)				
	-200	200	400	600	Mean
0	2.23	2.30	6.50	4.56	**3.90**
10	2.12	2.71	8.72	4.07	**4.41**
20	2.30	2.12	6.50	5.07	**4.00**
30	2.27	1.13	6.33	4.84	**3.64**
Mean	**2.23**	**2.07**	**7.01**	**4.64**	
LSD 0.05	Factor A =	0.35	Factor B =	0.21	A×B = *

Fig. 1. Effect of varying irrigation water sources on tissue Cu concentration (mg/kg) of vegetable species grown along the bank of Asa river in Ilorin, Nigeria
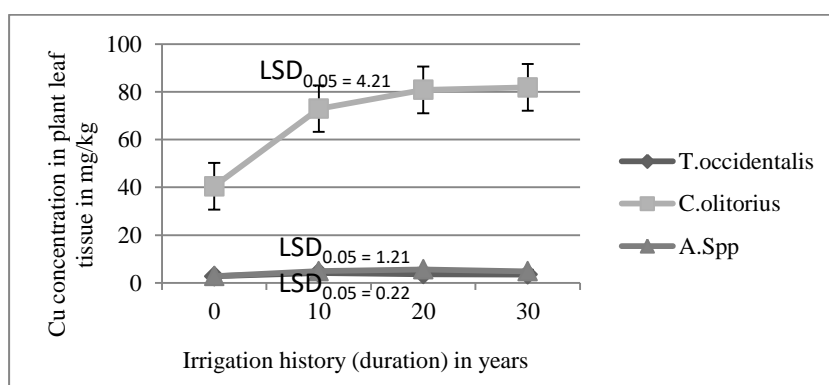

Fig. 2. Effect of varying irrigation history on tissue Cu concentration (mg/kg) of vegetable species grown along the bank of Asa river in Ilorin, Nigeria

On the other hand, plant species have a variety of capacities in removing and accumulating heavy metals. There are reports indicating that some plant species may accumulate specific heavy metals (Markert, 1993). This assertion is hereby corroborated by the current result showing *C. olitorius* as a good accumulator of Cu. Nevertheless, the uptake of heavy metals from the soil by plants depends on different factors, such as their soluble content, soil pH, fertilizers, and soil type (Lübben and Sauerberck, 1991). This may elicit result variations in studies of this kind.

Conclusion

From this study aimed at the determination of Asa river water quality for irrigation, it can be concluded that the Cu content at sampled locations was above the permissible level for irrigation water. Consequently, the continuous use of this river for irrigation by farmers has led to soil pollution with Cu metal and a subsequent transmission of non-permissible doses of Cu into C. *olitorius*, especially.

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