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# HEAVY METALS ACCUMULATION IN SOIL AND *AMARANTHUS CRUENTUS* L IRRIGATED WITH DYE EFFLUENT POLLUTED STREAM WATER IN ABEOKUTA, SOUTHWEST NIGERIA

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## ABSTRACT

This study evaluated the quality of *Amaranthus cruentus* irrigated with dye effluent polluted stream and water from a deep hand-dug surface well (well-water). It also assessed the levels of heavy metals including Manganese, Iron, Copper, Zinc and Chromium in soil and amaranths irrigated with the waters in two dry seasons. The results showed that the pH (9.67) and $NO_3^-$ (226.76 mg $L^{-1}$) contents of the dye effluent polluted stream were above maximum limits recommended for irrigation. Manganese, Fe, Cu, Zn and Cr in dye effluent polluted stream water were 0.013, 0.454, 0.041, 0.172 and 0.018 mg $L^{-1}$, respectively. Soil chemical properties increased significantly with dye effluent polluted stream water over well-water irrigation. Significant amount of metals accumulated in edible shoot of amaranths grown with dye polluted water compared with well-water. In 2010, shoot bioaccumulation of Mn, Fe, Cu, Zn and Cr were 122.47, 426.57, 10.60, 85.90 and 0.002 mg $kg^{-1}$. Bioaccumulations of the metals were 342.25, 518.22, 15.32, 344.31 and 0.003 mg $kg^{-1}$, respectively in 2011. Iron and Zn values in the vegetable were higher than FAO/WHO/FEPA permissible limits of 500 mg $kg^{-1}$ Fe and 60-100 mg $kg^{-1}$ Zn but Mn, Cu and Cr were within allowable limits. Irrigation with dye polluted stream water should be discouraged in this area to prevent build up of toxic metals in food chain.

*Keywords:* amaranths, bioaccumulation, dyeing, edible shoot, effluent, heavy metals

## INTRODUCTION

Contamination of soil and surface water bodies with effluent from dyeing industries is a rampant anthropogenic activity in most cities in Nigeria, particularly Abeokuta, southwestern Nigeria, where tie-dyeing of Adire/Kampala fabric is a major economic activity of the people. Textile dyeing requires large volume of water, as a result, dyeing industries are often sited close to regular source of water supply. The large volumes of effluent generated from the dyeing industries are discharged continuously into nearby gutters and drains which end up in streams and rivers causing pollution of the ecosystem. In some cases, the untreated effluents are being discharged directly into water bodies in the vicinities of the dyeing industries. It is also a common practice among the workers to wash dyed clothes directly in the shallow streams

and rivers around their industries (Plate 1). This type of human activities that lead to pollution of soil and surface waters appear to pose a direct and indirect threat to human health and the environment.

The dye effluents contains varieties of chemicals which include dyeing bases such as caustic soda, inorganic chlorine compounds and other oxidants such as hypochlorite of sodium, organic compound, as well as salts of heavy metals which when discharged on lands and water bodies can contaminate the environment (Ohioma *et al*., 2009). The toxic metals on entering the ecosystem may lead to geoaccumulation, bioaccumulation and biomagnifications (Prabu, 2009).

Cultivation of vegetables especially near streams and rivers is a common practice during the dry season in Abeokuta. Vegetables grown by farmers' during this period (December-March) along the banks of Asero stream where untreated dye effluents are discharged have the risk of been contaminated. Prolonged and continuous use of wastewater for growing these vegetables, other fodders and major crops may result in soil build up of heavy metals and salinity that may be phytotoxic (Ghafoor *et al*., 2004; Qadir and Oster, 2004; Khan *et al*., 2012).

The polluted water when used for irrigation can also have significant effects on soil properties in addition to bioaccumulation in crops beyond permissible limits for human consumption (Masona *et al*., 2011). Disposal of this textile effluents into irrigation canals can contribute to increased toxicity of metals in soil-plant systems because contaminated soils will inevitably result in the growth of contaminated vegetables (Jackson and Alloway, 1992; Rattan *et al*., 2005). They can also accumulate various chemicals and genotoxic compounds present in the soil (Griffith *et al*., 2001, Nupur *et al*., 2006). Toxic heavy metals consumed in unsafe concentrations through vegetables may lead to accumulation of these metals in kidney and liver (Sharman *et al*., 2009) leading to cardiovascular, nervous system, kidney and bone diseases (Jarup, 2003).

Amaranth is one of the most popular leafy vegetables consumed in Nigeria. It is an important vegetable crop for subsistence farmers in Africa (Grubben and Denton, 2004). It constitutes an essential component of human diet and act as a buffering agent for acidic substances produced during digestion process. Presently, there is little published information on the level of heavy metal accumulation in soil and amaranths irrigated with dye effluent polluted stream water especially in southwestern Nigeria. This study is therefore aimed at determining the levels of heavy metals in the irrigation water, irrigated soil, edible and non-edible portions of amaranths irrigated with dye effluent polluted stream water in this region.




**Plate 1: Dyers' at Asero stream washing dyed Adire/Kampala fabrics**

## MATERIALS AND METHODS

### *Study Area:*

The study was carried out at the bank of Asero stream, an adjoining stream to Adire/Kampala market in Abeokuta South Local Government Area of Ogun State, Southwest Nigeria, located at $7.17058^0$N, $3.37882^0$E and 125 m above sea level. In the study area, Asero stream has been a major source of irrigation water for farmers' for dry season cultivation of food crops mainly vegetables. This is due to the peri-urban nature of its location and suitability of the river bank for dry season vegetable production in addition to its proximity to the market.

### *Soil Sample Collection and Preparations*

Soil sampling was done by taken soil core from 0-15 cm and 15-30 cm depths with soil urger before the study and at harvesting of irrigated amaranths in February, 2010 and at the same time in 2011 dry season. Before the study, twenty (20) core samples were taken at each depth from the entire field to form composite samples. At crop harvest, five soil core samples were taken at each depth from the micro plots established as demonstration plots on the framers' field. Soil samples were also collected from field adjacent to the farmers' field as control. Core soil samples were bulked, air-dried and sieved with 2 mm mesh. The physicochemical properties as well as heavy metals (Cu, Zn, Fe, Mn and Cr) in the soil samples were determined in the laboratory using standard procedures (Okalebo, *et al*., 1993; Udo, *et al*., 2009).

### *Experimentation on Farmers' Fields*

Amaranths were grown during 2010 and 2011 dry seasons on the field of three farmers' who have irrigated their dry season vegetables with dye polluted stream water for more than five years. In each season, micro plot sizes of 1 m x 1 m were established in three replicates alongside that of the farmers. In a similar way, control plots were established on adjacent land and irrigated with water from a deep hand-dug surface well (well-water). Amaranths were sown by drilling seeds on the elevated beds at about 10 cm between rows. Plant population were monitored and thinned at two weeks after planting (WAP) to one plant per stand at a distance of about 4 cm within rows. Irrigation of each vegetable bed was done by applying 10 litres of dye polluted stream water taken directly from the stream three times per week. Weeding was done by uprooting weeds from vegetable beds and returning them *in-situ*. The vegetable was harvested at six weeks after planting (WAP) by taking ten (10) plant samples randomly selected from a quadrant of 0.5 m by 0.5 m placed centrally on the plot. After harvesting, the biomass was separated into shoots (edible) and roots (non-edible) parts. The amaranths were later water cleaned with fresh water as would be done during cooking, air dried and later oven dried at $60^o$ C to constant weight, milled for laboratory analyses.

### *Sampling and Analyses of Stream Water*

Water samples from the dye polluted Asero stream was taken for chemical analysis. Sampling was done in January 2010, when farmers have started using the stream water for their dry season cropping. Water sample from nearby well which serves as the control was also taken fresh at the same time for laboratory analysis. Water samples were taken in 2 litres plastic containers previously washed with liquid detergent and rinsed with distilled water followed by deionized water. The samples were kept in cooler containing ice block and transported to the laboratory where they were stored in refrigerator at $4^0$ C prior to analysis. The physicochemical qualities of the water samples were analyzed. The pH was measured with pH meter using glass electrode. Conductivity/Total Dissolved Solid (TDS) meter was used to measure the Electrical Conductivity (EC) and Total Dissolved Solid (TDS). Chemical Oxygen Demand (COD) was determined using the titrimetric method. Dissolved Oxygen (DO) was determined before and after an incubation period of five days in the dark at $20^o$ C by the Alkaline-Azide modification of Winkler's method. The

Biological Oxygen Demand (BOD) was estimated from the amount of DO present in each sample before and after the incubation periods.

Sulphate was determined by turbidimetric method by reading the absorbance of samples on a UV-Visible spectrophotometer at 425 nm. Phosphate was determined by Vanado-Molybdo-Phosphoric acid colorimetric method by reading the absorbance of samples on a UV-Visible spectrophotometer at 470 nm. Nitrate was measured by the phenoldisulphonic method, reading the absorbance of samples on spectrophotometer at 410 nm after the development of colour. The concentrations of sodium and potassium were measured using flame photometer. Magnesium as well as heavy metals (Mn, Fe, Zn, Cu and Cr) in the water samples was estimated with Buck Scientific 210 VGP Atomic Absorption Spectrophotometer (AAS) after passing the filtrate through 125 mm whatman filter paper. All methods followed procedures as explained in APHA (2005).

***Analyses of Soils collected from the Farmers' field before and after Cropping***

The soil pH was determined with the use of glass electrode pH-meter using soil water ratio of 1:2. Organic Carbon by Walkley and Black method using dichromate ($K_2Cr_2O_7$) as oxidizing agent. The soil total nitrogen was determined following micro Kjedahl digestion method. Available phosphorus was also determined colorimetrically using Bray-1-method. The exchangeable bases in the soil was extracted with 1N Ammonium acetate (pH 7.0), calcium and magnesium were determined with atomic absorption spectrophotometer (AAS) while potassium and sodium were determined on a flame photometer. These analyses followed procedures in Okalebo, *et al*., (1993) and Udo, *et al*., (2009). Exchangeable acidity ($H^+$) was estimated by extracting with 1N KCl and determined by NaOH titration. Effective cation exchange capacity (ECEC) was estimated by summing the exchangeable bases plus exchangeable acidity. Concentrations of heavy metals including Cu, Zn, Mn, Fe and Cr in the soil samples were analyzed using perchloric acid digestion method with the use of atomic absorption spectrophotometer (AAS) Buck 210 VGP model (Udo, *et al*., 2009). The metals were determined at their characteristic wavelength after calibrating the equipment, Cu at 324.5 nm, Zn at 213.9 nm, Mn at 279.5 nm, Fe at 386.7 nm, and Cr at 357.5 nm respectively. Particle size distribution was determined by the hydrometer method (Bouyoucos, 1951).

***Heavy Metal Analyses in Amaranths***

Plant parts previously milled were digested for 1 hour 30 minutes at 150$^o$ C by weighing 0.5 g of samples into digestion tubes followed by addition of nitric and perchloric acid (2:1). The temperature of the digest was raised to 230$^o$ C after which 2 ml of hydrochloric acid and distilled water were added and digested for another 30 minutes. The digests were allowed to cool and washed into 50 ml volumetric flasks and made up to mark with distilled water. Heavy metals were then determined on Buck Scientific 210 VGP AAS.

***Data Analysis***

All data collected were analyzed statistically following SAS procedure (SAS, 1998). The significance of treatment means was determined by using Duncan Multiple Range Test (DMRT) at 5 % probability.

**RESULTS AND DISCUSSION**

The physicochemical properties of the two sources of irrigation water used in this study are presented in Table 1. The pH of the well water was near neutral (7.10) while that of the dye polluted stream was alkaline (9.67). The Electrical Conductivity (EC) of the well water was 516 µs $cm^{-1}$ and that of the dye polluted stream was 246 µs $cm^{-1}$. Total dissolved solid (TDS) was 126 mg $L^{-1}$ in the well water and 280 mg $L^{-1}$ in the dye polluted stream, chemical oxygen demand (COD) was 0.10 mg $L^{-1}$ and 0.12 mg $L^{-1}$ in the well and dye polluted stream water,

**Table 1: Physicochemical properties of well and dye polluted stream water samples used for irrigation of Amaranths**

| Parameters | Well Water | Dye Polluted Stream Water | WHO/FAO/ FEPA Limit for irrigation |
|---|---|---|---|
| pH | 7.10 | 9.67 | 6 – 9 |
| EC ($\mu s\ cm^{-1}$) | 516 | 246 | 600 |
| TDS ($mg\ L^{-1}$) | 126 | 280 | 2000.0 |
| COD($mg\ L^{-1}$) | 0.10 | 0.12 | 1000.0 |
| DO ($mg\ L^{-1}$) | 2.98 | 2.09 | 5.0 |
| BOD($mg\ L^{-1}$) | 0.15 | 0.11 | 50.0 |
| $SO_4^{2-}$($mg\ L^{-1}$) | 29.68 | 19.36 | 250.0 |
| $PO_4^{3-}$($mg\ L^{-1}$) | 0.05 | 0.14 | 5.0 |
| $NO_3^-$ ($mg\ L^{-1}$) | 22.68 | 226.76 | 45.0 |
| K ($mg\ L^{-1}$) | 16.76 | 10.74 | NE |
| Mg ($mg\ L^{-1}$) | 2.43 | 2.72 | NE |
| Na ($mg\ L^{-1}$) | 184 | 292 | NE |
| Mn ($mg\ L^{-1}$) | 0.009 | 0.013 | 0.2 |
| Fe ($mg\ L^{-1}$) | 0.121 | 0.454 | 0.3 |
| Cu ($mg\ L^{-1}$) | 0.038 | 0.041 | 0.5 |
| Zn ($mg\ L^{-1}$) | 0.110 | 0.172 | 1.0 |
| Cr ($mg\ L^{-1}$) | 0.004 | 0.018 | 0.1 |

NE = Not Established

Federal Environmental Protection Agency (FEPA, 1991) Nigeria

respectively. Dissolved Oxygen (DO) was a bit higher in well water (2.98 mg $L^{-1}$) than in the dye polluted stream water (2.09 mg $L^{-1}$). Biological Oxygen Demand (BOD) content of the well water was 0.15 mg $L^{-1}$ and that of the dye polluted stream was 0.11 mg $L^{-1}$. The pH of dye polluted stream used for irrigation of amaranths was higher than the critical limit of pH 6-9 allowable by WHO/FAO/FEPA for irrigation purposes. The higher pH value of the dye polluted stream over that of the well water is an indication of alkaline nature of dye effluent discharged into the stream. The salt content, EC of the well water indicates that the value is within the allowable limit recommended for irrigation. However, lower EC in the dye polluted stream could be due to dilution of the dye effluent on discharge to larger volume of water in the stream. When EC values of irrigation water exceeds 300 µs $cm^{-1}$, the germination of crops would be affected and could result in yield reduction (Lokhande *et al*., 1996). The TDS of the two sources of irrigation water were below the critical limit and as such suitable for irrigation. The COD, DO and BOD of the irrigation sources also indicated its suitability for irrigation.

The concentration of Sulphate ($SO_4^{2-}$) in the well water (29.68 mg $L^{-1}$) was higher than in the dye polluted stream (19.36 mg $L^{-1}$). Meanwhile phosphate ($PO_4^{3-}$) level was lower in the well water (0.05 mg $L^{-1}$) than in the dye polluted stream (0.14 mg $L^{-1}$). Nitrate ($NO_3^-$) content was low in well water (22.68 mg $L^{-1}$) and very high in the dye polluted stream water (226.76 mg $L^{-1}$). The potassium (K) content of the well water was 16.76 mg $L^{-1}$ while that of the dye polluted stream was lower (10.74 mg $L^{-1}$). The magnesium (Mg) levels were 2.43 mg $L^{-1}$ and 2.72 mg $L^{-1}$ in well and dye polluted stream water, respectively. The concentration of dissolved sodium (Na) was lower in the well (184 mg $L^{-1}$) than in the dye polluted stream (292 mg $L^{-1}$). Sulphate and phosphate values were below limits recommended by WHO/FAO/FEPA and therefore suitable for growing vegetable. The high $NO_3^-$ concentration beyond the allowable

limit of 45 mg $L^{-1}$ by WHO/FAO/FEPA in dye polluted stream showed that such water is not of good quality for irrigation purpose. The high nitrate may be due to presence of indigo ($C_{16}H_{10}N_2O_2$) family, a derivative of vat dyes in the effluent which on decomposition can form urea [$CO(NH_2)_2$]. According to Ganguly and Maiti (2004) high nitrate concentration in sewage water was due to presence of urea, which is a major source of nitrogen in wastewater. The lower K content in dye polluted water than well water could be due to dilution of the effluent on reaching larger volume of water in the stream. The higher levels of Mg and Na in the dye polluted stream on the other hand could be due to their concentrations in the dye effluent released into the stream. In particular, higher Na content may be largely due to presence of sodium hydrosulphite ($Na_2S_2O_4$) a reducing agent used in dyeing process for improving solubility of vat dyes.

Heavy metals including manganese (Mn) concentration in the well water sample was 0.009 mg $L^{-1}$ and slightly higher (0.013 mg $L^{-1}$) in the dye polluted stream sample. Iron (Fe) was low in the well water (0.121 mg $L^{-1}$) and very high in dye polluted stream (0.454 mg $L^{-1}$). The copper (Cu) content was 0.038 mg $L^{-1}$ in well water and 0.041 mg $L^{-1}$ in the dye polluted stream. zinc (Zn) concentration was 0.110 mg $L^{-1}$ in well water sample and 0.172 mg $L^{-1}$ in dye polluted stream water. The chromium (Cr) level in the well water was 0.004 mg $L^{-1}$ and 0.018 mg $L^{-1}$ in dye polluted stream water. The heavy metal values were generally below the maximum permissible limits prescribed for irrigation and land disposal except for Fe in the dye polluted stream with value above 0.3 maximum limits allowable for discharge into rivers by WHO/FAO/FEPA. This can be attributed to high level of Fe in the untreated dye effluent released into the stream. Continuous use of the dye polluted stream water for irrigation of leafy vegetable such as amaranths can lead to elevated level of Fe in the crop among other metals. Long term application of poor quality of effluent/wastewater for crop production can cause accumulation of some toxic metals in soils above critical limits which is harmful for soil health and may lead to elevated levels of heavy metals in crop plants (Nauman and Khalid, 2010).

The physicochemical soil properties of the farmers' field before the study as revealed in Table 2 showed that the pH of the soil were slightly acidic with pH 6.9 and 6.8 in 0-15 cm and 15-30 cm depths, respectively. Total N was 0.15 % and 0.09 % at 0-15 cm and 15-30 cm soil depths. Organic carbon was 1.75 % at the upper soil layer and 0.87 % down the soil profile. Available P was more in the 15-30 cm depth (8.83 mg $kg^{-1}$) than in the upper 0-15 cm depth (5.54 mg $kg^{-1}$). Exchangeable Ca and Mg were higher in upper 0-15 cm soil layer than 15-30 cm depth, but Na and K contents had their highest values at 15-30 cm than in the upper soil layer. Exchangeable acidity of the soil was 0.05 cmol (+) $kg^{-1}$ at both depths. Effective CEC was 6.29 cmol (+) $kg^{-1}$ in 0-15 cm depth and 5.75 cmol (+) $kg^{-1}$ in 15-30 cm layer while base saturation were 98.27 % and 99.13 % at the upper and lower layers, respectively. The concentration of Cu, Fe and Cr were higher in the lower soil depth than upper 0-15 cm depth. Zinc and Mn on the other hand had values of 2.78 and 1.67 mg $kg^{-1}$ as well as 42.51 and 25.40 mg $kg^{-1}$ at the 0-15 cm and 15-30 cm depths, respectively. The higher concentrations of plant nutrients (P, Na, K) and heavy metals (Cu, Fe, Cr) in the lower soil layer than in the upper layer could be due to leaching loss in sandy soil with low clay content. The soil samples had large proportion of sand particle, very low silt and fairly low clay contents with sandy loam texture. Tables 3 & 4 showed soil properties of farmers' field after two cropping seasons of amaranths with dye polluted stream water and well water. Generally, in the two dry seasons, soil chemical properties including pH, Total N, organic carbon, available P, Ca, Mg, Na, K as well as ECEC were significantly ($p \leq 0.05$) contaminated at the upper soil layer (0-15 cm) in field irrigated with dye polluted stream water compared with well-water.

**Table 2: Physicochemical properties of soil collected from farmers' field at Asero stream bank before cropping**

| | Soil depth (cm) | |
|---|---|---|
| **Soil Properties** | **0 – 15** | **15 -30** |
| pH ($H_2O$) | 6.9 | 6.8 |
| Total N (%) | 0.15 | 0.09 |
| Organic carbon (%) | 1.75 | 0.87 |
| Available P (mg $kg^{-1}$) | 5.54 | 8.83 |
| Ca (cmol (+) $kg^{-1}$) | 4.14 | 3.79 |
| Mg (cmol (+) $kg^{-1}$) | 1.63 | 1.04 |
| Na (cmol (+) $kg^{-1}$) | 0.24 | 0.31 |
| K (cmol (+) $kg^{-1}$) | 0.23 | 0.56 |
| H+Al (cmol (+) $kg^{-1}$) | 0.05 | 0.05 |
| ECEC (cmol (+) $kg^{-1}$) | 6.29 | 5.75 |
| Base saturation (%) | 98.27 | 99.13 |
| Cu (mg $kg^{-1}$) | 0.41 | 1.25 |
| Zn (mg $kg^{-1}$) | 2.78 | 1.67 |
| Fe (mg $kg^{-1}$) | 9.68 | 10.84 |
| Mn (mg $kg^{-1}$) | 42.51 | 25.40 |
| Cr (mg $kg^{-1}$) | 5.67 | 7.09 |
| Sand (%) | 76.00 | 77.20 |
| Silt (%) | 6.81 | 6.00 |
| Clay (%) | 17.20 | 16.80 |
| Textural Class | Sandy loam | Sandy loam |

irrigated soil (Table 3). The soil reaction (pH) of the root zone was slightly alkaline (pH 7.20) in 2010 and the alkalinity increased to pH 8.80 by 2011 in soil irrigated with dye polluted stream water. However, pH of the lower soil layer (15-30 cm) was lower in both seasons with pH 6.97 and pH 7.90 compared to their corresponding pH values in the upper soil layers. Unlike field irrigated with dye polluted steam water, well water irrigated field were slightly acidic in both seasons, with pH 6.87 and pH 6.92 in 2010 and 2011 dry seasons, respectively. The increased pH or low acidity of soil irrigated with dye polluted stream water could be largely attributed to alkaline nature of the source of water used for irrigation. This reflects that dye polluted stream water has a positive effect on the irrigated soil as it lowered acidity and this encouraged nutrients availability (Masona *et al*., 2011). The nutrient elements in soil irrigated with dye polluted water were higher in the top 0-15 cm than 15-30 cm depth except for Mg in 2010. This could be due to its presence in the dye polluted water or leaching loss in soil with low clay content. Field irrigated with well water showed higher available P (9.19 c mol (+) $kg^{-1}$), Ca (3.71 c mol (+) $kg^{-1}$), Mg (0.94) c mol (+) $kg^{-1}$, Na (0.19 c mol (+) $kg^{-1}$), K (0.20 c mol (+) $kg^{-1}$), ECEC (5.09 c mol (+) $kg^{-1}$) and base saturation (99.02 %) in lower soil layer (15-30 cm) than in upper layer in 2010 dry season. In the following dry season (2011), only Ca (3.82 c mol (+) $kg^{-1}$), Mg (0.96 c mol (+) $kg^{-1}$), K (0.21 c mol (+) $kg^{-1}$), ECEC (5.21 c mol (+) $kg^{-1}$) and base saturation percentage (99.6 %) maintained it higher concentrations in 15-30 cm soil depth.

The mean concentrations of Cu, Zn, Fe, Mn and Cr in the soil irrigated with dye polluted stream water were significantly higher than well-water irrigated soil in the two dry seasons and at both soil depths (Table 4). In the upper layer (0-15 cm) of soil irrigated with dye polluted stream water, Cu accumulation increased from 0.53 mg $kg^{-1}$ in 2010 to 3.78 mg $kg^{-1}$ in 2011, Zn

**Table 3: Effect of dye polluted stream water irrigation on chemical soil properties of Farmers' field at Asero stream bank after two dry seasons of cropping**

| Soil properties | 2010 Dry season | | | | 2011 Dry season | | | |
|---|---|---|---|---|---|---|---|---|
| | Polluted water | | Well water | | Polluted water | | Well water | |
| | 0-15cm | 15-30cm | 0-15cm | 15-30cm | 0-15cm | 15-30cm | 0-15cm | 15-30cm |
| pH ($H_2O$) | 7.20a | 6.97a | 6.87b | 6.43b | 8.80a | 7.9a | 6.92b | 6.57b |
| Total N (%) | 0.18a | 0.10a | 0.14b | 0.08b | 0.57a | 0.48a | 0.16b | 0.15b |
| Organic carbon (%) | 1.35a | 0.88a | 1.19b | 0.76b | 1.42a | 1.39a | 1.21b | 1.13b |
| Available P (mg $kg^{-1}$) | 15.90a | 12.60a | 3.46b | 9.91b | 16.87a | 13.07a | 4.28b | 4.16b |
| Ca (cmol (+) $kg^{-1}$) | 4.81a | 4.55a | 2.96b | 3.71b | 11.4a | 5.07a | 3.02b | 3.82b |
| Mg (cmol (+) $kg^{-1}$) | 1.41a | 1.50a | 0.82b | 0.94b | 1.70a | 1.57a | 0.85b | 0.96b |
| Na (cmol (+) $kg^{-1}$) | 0.37a | 0.33a | 0.17b | 0.19b | 0.43a | 0.37a | 0.21b | 0.20b |
| K (cmol (+) $kg^{-1}$) | 0.65a | 0.58a | 0.18b | 0.20b | 0.68a | 0.67a | 0.19b | 0.21b |
| H+Al (cmol (+) $kg^{-1}$) | 0.07a | 0.04a | 0.06a | 0.05a | 0.03a | 0.02a | 0.02a | 0.02a |
| ECEC (cmol (+) $kg^{-1}$) | 7.31a | 7.00a | 4.19b | 5.09b | 14.24a | 7.70a | 4.29 | 5.21b |
| Base saturation (%) | 99.04a | 99.43a | 98.57a | 99.02a | 99.79a | 99.74a | 99.53a | 99.62a |

Means within the same depth in the same row followed by the same letters are not significantly different ($p \leq 0.05$) according to Duncan's Multiple Range Test

**Table 4: Effect of dye polluted stream water irrigation on soil heavy metals of Farmers' field at Asero stream bank after two dry seasons of cropping**

| Soil properties | 2010 Dry season | | | | 2011 Dry season | | | |
|---|---|---|---|---|---|---|---|---|
| | Polluted water | | Well water | | Polluted water | | Well water | |
| | 0-15cm | 15-30cm | 0-15cm | 15-30cm | 0-15cm | 15-30cm | 0-15cm | 15-30cm |
| Cu (mg $kg^{-1}$) | 0.53a | 0.41a | 0.28b | 0.34b | 3.78a | 3.31a | 0.35b | 0.39b |
| Zn (mg $kg^{-1}$) | 2.19a | 1.96a | 1.38b | 1.30b | 9.65a | 7.10a | 1.54b | 1.31b |
| Fe (mg $kg^{-1}$) | 11.92a | 10.06a | 8.78b | 7.99b | 27.50a | 17.5a | 9.13b | 8.94b |
| Mn (mg $kg^{-1}$) | 54.90a | 36.75a | 33.50b | 31.87b | 64.50a | 51.02a | 34.94b | 32.15b |
| Cr (mg $kg^{-1}$) | 7.15a | 6.66a | 6.78b | 5.99b | 8.33a | 7.20a | 6.81b | 5.95b |

Means within the same depth in the same row followed by the same letters are not significantly different ($p \leq 0.05$) according to Duncan's Multiple Range Test

increased from 2.19 mg $kg^{-1}$ in 2010 to 9.65 mg $kg^{-1}$ in 2011, Fe increased from 11.92 mg $kg^{-1}$ in 2010 to 27.50 mg $kg^{-1}$ in 2011, Mn increased from 54.90 mg $kg^{-1}$ in 2010 to 64.50 mg $kg^{-1}$ in 2011 while Cr which was 7.15 mg $kg^{-1}$ in 2010 increased slightly to 7.20 mg $kg^{-1}$ in the following dry season. Similar studies of Mapanda *et al*., (2005) on vegetables revealed increased concentrations of Cu, Zn and Cr among other metals in soils irrigated continuously with wastewater. The increased soil accumulation of metals with dye polluted stream water can be attributed to its chemical constituents including organic matter via-à-vis the pH. Masona *et al*. (2011) have also reported significant effect of wastewater irrigation on soil properties. Over the dry season periods higher metal contamination occurred in the upper soil profile than in lower layers of soil irrigated with both well and dye polluted stream water except Cu in well water irrigated soil. The Cu content was 0.28 mg $kg^{-1}$ at 0-15 cm and 0.34 mg $kg^{-1}$ at 15-30 cm in 2010. In the following season soil Cu levels were 0.35 mg $kg^{-1}$ and 0.39 mg $kg^{-1}$ at 0-15 cm and 15-30 cm, respectively.

Higher soil chemical properties in upper soil layer (0-15 cm) compared with 15-30 cm depth of soil irrigated with dye polluted stream water indicated presence of the chemical elements in the dye polluted stream water which enhanced their deposits in the first layer of soil contact. However, availability of substantial amount of nutrient elements at 15-30 cm depth more than at upper 0-15 cm in

soil irrigated with well water could be due to leaching of nutrients in soil with low clay content. For the two sources of irrigation water and in the two dry seasons, heavy metals accumulated more in the upper than lower soil layers, with soil that received dye polluted stream water been significantly ($p \leq 0.05$) higher than well water irrigated soil. Hence, a combination of soil and dye effluent composition factors might be responsible for the higher accumulation of heavy metals in the soils.

Long term application of wastewater for irrigation has been reported to result in increased heavy metal concentrations in soils (Masona *et al*., 2011) and could be above critical limits which is harmful for soil health and may lead to elevated levels of heavy metals in crop plants Nauman and Khalid, (2010). The higher level of Cu at 15 - 30 cm depth indicates that Cu is more mobile than other heavy metals in these soils. The dominance of sand in the soils with low activity clay and silt contents not only contributed to low heavy metals in soils irrigated with fresh well water, but also led to low retention of anthropogenically introduced metals in soil irrigated with the dye polluted stream water (Abulude, 2005; Uwah, 2009).

**Heavy metal concentrations in Amaranths irrigated with dye polluted steam water**

Heavy metals accumulation in amaranths irrigated with dye polluted steam and well-water are presented in Table 5. Heavy metals accumulation were significantly higher ($p \leq 0.05$) in amaranth irrigated with dye polluted stream water than those grown with well water in both seasons. Generally, more metal accumulated in the edible shoots of amaranth than roots except Cr. Only Fe in amaranth irrigated with well-water showed roots content being higher than shoots which is an indication of poor translocation. Heavy metal concentrations in amaranths tissues irrigated with dye polluted stream water were higher in 2011 than in previous dry season. The shoot content of Mn increased from 122.47 mg $kg^{-1}$ in 2010 to 342.25 mg $kg^{-1}$ in 2011, Fe from 426.57 mg $kg^{-1}$ in 2010 to 518.22 mg $kg^{-1}$ in 2011, Cu from 10.60 mg $kg^{-1}$ in 2010 to 15.32 mg $kg^{-1}$ in 2011, Zn increased from 85.90 mg $kg^{-1}$ in 2010 to 344.31 mg $kg^{-1}$ in 2011 and Cr from 0.002 mg $kg^{-1}$ in 2010 to 0.003 mg $kg^{-1}$ in 2011, respectively. Our study corroborates with studies of Arora *et al*. (2008) showing elevated levels of heavy metals in edible parts of food crops with continuous wastewater irrigation. Unlike dye polluted stream water irrigated amaranth, the tissue concentrations of metals in edible shoot of amaranth irrigated with well- water gave declined values except for Fe which increased from 240.02 mg $kg^{-1}$ in 2010 to 285.54 mg $kg^{-1}$ in 2011. Also Zn shoot value slightly increased from 44.35 mg $kg^{-1}$ in

**Table 5: Effect of dye polluted stream water irrigation on heavy metal levels in shoot and root of *Amaranthus cruentus* L.**

| Heavy metal (mg $kg^{-1}$) | 2010 Dry season | | | | 2011 Dry season | | | |
|---|---|---|---|---|---|---|---|---|
| | Polluted water | | Well water | | Polluted water | | Well water | |
| | Shoot | Root | Shoot | Root | Shoot | Root | Shoot | Root |
| Mn | 122.47a | 54.48a | 47.53b | 33.47b | 342.25a | 96.98a | 42.48b | 30.06b |
| Fe | 426.57a | 422.53a | 240.02b | 351.95b | 518.22a | 439.18a | 285.54b | 365.44b |
| Cu | 10.60a | 7.40a | 7.80b | 4.68b | 15.32a | 8.43a | 5.16b | 2.31b |
| Zn | 85.90a | 52.47a | 44.35b | 28.18b | 344.31a | 20.74a | 44.66b | 15.06b |
| Cr | 0.002b | 0.003a | 0.001b | 0.002a | 0.003a | 0.004a | 0.001b | 0.002b |

Means of the same part in the same row followed by the same letters are not significantly different ($p \leq 0.05$) according to Duncan's Multiple Range Test

2010 to 44.66 mg $kg^{-1}$ in 2011. In both dry seasons, edible shoot of the amaranth had lower levels of Mn, Cu and Cr than the maximum permissible limits of 425, 40-73 and 1.3 mg $kg^{-1}$, respectively in vegetable proposed by WHO/FAO (1984) but still significantly higher than contents in those amaranths irrigated with well-water. Higher concentrations of Mn, Fe, Cu, Zn and Cr in the tissues of amaranths irrigated with dye polluted stream water than in well-water irrigated amaranths indicates the presence of heavy metals in the dye polluted stream water which resulted in contamination of soil and the amaranth. This finding is in agreement with previous studies of Zia *et al*. (2008) and Singh *et al*. (2010) who also found higher concentration of heavy metals in wastewater irrigated vegetables compared to clean water irrigated ones. The significant contribution of dye polluted stream water to metal accumulation in the seasonal amaranth showed that the dye polluted Asero stream is not only a source of nutrients to farmers' field but also an elevator of heavy metals in receiving soils (Singh *et al*., 2004) which are translocated to edible part of the amaranth and could impair its nutritional quality. Similar study by Hossain *et al*. (2010) reported that discharge of industrial wastewater in agricultural lands can degrade the quality of crops. The higher concentration of Fe and Cr in roots than shoots of amaranth irrigated with well water is an indication of poor translocation of the metals to upper plant parts in fresh well water irrigated soil (Zia *et al*., 2008). Unfortunately, the levels of Fe and Zn in the edible shoot were higher than 425 mg $kg^{-1}$ Fe and 60-100 mg $kg^{-1}$ Zn considered being toxic in shoot of vegetables by FAO/WHO (1984), WHO (2003). The elevated concentration of the metals can lead to contamination of food chain, since one of the important dietary uptake pathways could be through vegetables irrigated with contaminated wastewater (Farooq *et al*., 2008).

## CONCLUSION

Continuous use of dye polluted stream water for irrigation purpose showed significant increase in heavy metal levels in farmers' field and accumulation of the metals in edible shoot of amaranths. Dye polluted stream water irrigated amaranths in the second dry season accumulated significant amount of Fe and Zn which were above the permissible limit set by FAO/WHO/FEPA, indicating bioaccumulation in edible shoots and might pose health threat to consumers. The researchers therefore recommend that the unwholesome attitude of discharging dye effluent and washing of dyed fabrics in streams used by farmers as the only source of irrigation in the dry season should be discouraged to avoid entrance of toxic metal in food chain.

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