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Levels of Some Trace Metals in the Fadama Soils and Pepper (*Capsicum annuum*) Along the Bank of River Challawa, Nigeria

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Abstract: The levels and distribution of Pb, Cr and Cu in the soils and pepper (*Capsicum annuum*) on the bank of River Challawa were investigated. The metal levels, expressed in mg kg^{-1} Dry Weights (DW) in the ranges: 60.00-143.30 for Pb (mean 114.79), 104.20-230.00 for Cr (mean 181.66) and 58.30-207.50 for Cu (mean 248.59) are obtained in soil samples; while 11.33-27.00 for Pb (mean 18.90), 10.40-35.10 for Cr (mean 20.04) and 7.56-21.07 for Cu (mean 14.52) are obtained in pepper samples. The relationship of metals was also examined for dependency upon some soil factor through the use of correlation analysis. Also, the results show the presence of correlation between metals in soil and pepper, which indicate possible transfer of these metals into the food chain. This has indirectly caused the accumulated of these heavy metals in the agricultural soils through irrigation and subsequently in the pepper planted in them, such that their concentrations in the soils and pepper (except Cu in pepper) exceed the recommended permissible limits.

Key words: Assessment, heavy metals, pepper, soil

INTRODUCTION

Fadama is a Hausa word meaning the seasonally flooded or floodable plains along major Savannah Rivers and/or depressions on the adjacent low terraces (Adeyeye, 2005). Fadama utilization has been a major feature of the agricultural, food, economic and demographic experience of the Nigerian dry belt. Fadama soils are used for agriculture and allows the production of crops throughout the year and are therefore of economic benefits to the local communities. During this period the usual cereal-based farming system is replaced with vegetables such as carrots, tomatoes, onions, spinach and pepper.

The rationale for resource utilization here hinges on the availability of valuable agricultural resources in a zone where rain fed agricultural prospects are poor due to the small and erratic nature of rainfall and endemicity of drought. Of a particular threat to Fadama or lowland irrigation crops in dryland areas are industrial effluents from factories and manufacturing facilities which contaminate irrigation channels.

Recently pollution of general environment has increasingly gathered a global interest. In this respect, contamination of agricultural soils with heavy metals has always been considered a critical challenge in scientific community (Faruk *et al*., 2006). Heavy metals are generally present in agricultural soils at low levels. Due to their cumulative behaviour and toxicity, however, they have a potential hazardous effect not only on crop plants but also on human health (Das *et al*., 1997).

Nigeria's production of pepper is incomparable with other countries, although there is a kind of specialization in Niger and Benin for some vegetables. This specialization is caused by various agro-climatic constraints. Pepper is essentially an out of season crop, practiced on hydro-agricultural lands, produced is concentrated in the North of Benin, Nigeria and Cameroon and in the South of Sahelian

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countries, more specifically in the dry tropical zone. In this light, the greater part of pepper production in Nigeria is undertaken in the north of the country, in Kaduna, Kano, Jigawa, Katsina, Sokoto, Plateau and Bauchi states. The natural features of these regions, especially the presence of flood-prone plains and river basins and above all the development of vast irrigated lands, create conditions that greatly favour the development of this crop. The annual production of pepper/sweet pepper is estimated 251,230 tons in 1995/96. This estimate for Nigeria is for the states mentioned above and the production level is expected to rise annually coupled with the rising population and increased farming activities source (Agricultural Project Monitoring and Evaluation Unit, Kaduna, 1996).

A survey of the literature shows that there is some information on the levels of heavy metals in water and sediments of Challawa River. However, there are no reports on the levels of trace metals in vegetable crops e.g., pepper grown along the Challawa river bank. Thus, there is the need to carry out extensive assessment on the vegetable crops grown in the vicinity of the Challawa River, especially pepper in order to have some insight into impact of tanning operations on vegetable crops grown on the bank of the river. Therefore, this research was initiated to determine the level of trace metals (Pb, Cu and Cr) in peppers and Fadama soils along the bank of Challawa River in Kano, Nigeria as a result of indiscriminate release of toxic effluents discharge by the tanneries into the river.

MATERIALS AND METHODS

Analytical reagent (AnalaR) grade chemicals and distilled water were used throughout the study. All glassware and plastic containers used were washed with detergent solution followed by 20% (v/v) concentrated Trioxonitrate (IV) acid and then rinsed with water and finally with distilled water (Audu and Lawal, 2005).

Sample Collection

The study was carried out in between February and April, 2006. Thirty two harvested pepper (*Capsicum annum*) and 16 surface soil samples were collected from the study area, packaged in paper bags and labeled. These were immediately transported to the laboratory for processing and preservation. However, there was no harvested pepper at the control site at the time of sampling, hence 16 soil samples were collected from that site. Only fresh vegetables (pepper) in prime condition were collected in order to produce good quality dried products (Audu and Lawal, 2005).

Digestion of Samples

Soil samples from each site was homogenized and air-dried in a circulating air in the oven at 30°C to a constant weight and passed through a 2 mm sieve. Five gram of soil samples were placed in 100 mL beaker. Three milliliter 30% hydrogen peroxide was added following a previously described procedure by Shriadah (1999). This was left to stand for 60 min until the vigorous reaction ceased. Seventy five milliliter of 0.5 M solution of HCl was added and the content heated gently at low heat on hot plate for about 2 h. The digest was then filtered into 50 mL standard flask. Triplicate digestion of each sample together with blank was also carried out. Then the quantitation of metallic content of digested samples was carried out with the flame atomic absorption spectrophotometry model AA 650.

The pepper samples were washed with tap water (Burton and Patterson, 1979) and thereafter with distilled water, sliced in nearly uniform size to facilitate drying of the pieces at the same rate and then dried in an oven at 105°C for 24 h, until they were brittle and crisp (APHA, 1992). At this stage, no microorganism can grow and care was taken to avoid any source of contamination. The dried samples were grinded into fine particles using clean acid washed mortar and pestle. The procedure according to Awofolu (2005) and Adeyeye (2005) was used for digestion of plant sample.

Determination of Some Physico-Chemical Parameters of Roadside Soil

Soil pH was measured in a 1:2 soil to water ratio (Herdershot *et al*., 1993). Particle size distribution was determined by the hydrometer method as described by Bougoucos (1951). Soil organic matter was determined by the wet oxidation method of Walkley and Black (1934).

Quality Assurance

Quality control test was conducted on soil and plant samples in order to evaluate the experimental procedures and efficiency of atomic absorption spectrophotometer. This was done by spiking the pre-digested soil and pepper samples with multielement metal standard solution (0.5 mg L^{-1} of Pb and Cu and 5 mg L^{-1} of Cr). The spiked samples were then digested as the sample procedure used for soil and pepper sample as described above.

RESULTS AND DISCUSSION

Method Validation

The validity of the procedures used for sample treatment and analysis was tested by spiking experiment. The recoveries of soil were 96.0, 90.0 and 96.8% for Pb, Cu and Cr, respectively. The recoveries for those of pepper sample were 96.3, 92.8 and 98.6% Pb, Cu and Cr, respectively. Recoveries from pepper samples were generally higher than soil samples with Cr in pepper sample having the highest recovery overall. The recovery results were in good agreement with expected values. Therefore the recovery test and reproducibility of the method were found satisfactory to validate the experimental protocol.

Soil Physicochemical Properties

Generally, all samples from the study sites were dominated by high average % sand fractions followed by % clay and finally % silt as shown on Table 1. Soil pH varied from 5.93-6.67, indicative of slightly acidic environment. Organic matter (%) was generally high in the study area.

Concentration of Heavy Metals in Soils

Highest concentration of Pb, Cu and Cr were observed in the study area. Analysis of variance between heavy metals in study and control area revealed significant difference ($p<0.05$). The trend of occurrence of heavy metals in study areas revealed; Cu > Cr > Pb while the control area revealed; Cu > Pb > Cr (Table 2). As Table 3 show, positive correlation was found between Cr and Pb in soil samples from the study area. This indicates common source of these metals. Negative correlations were found between Cu and Pb, Cu and Cr in soils. This also could indicate different source of these metals in soils of the study area.

Table 1: Physicochemical properties of the soils

Parameters	Min.	Max.	Mean±SD
Study site (n = 16)			
pH	4.40	6.90	5.93±0.67
OM (%)	2.20	2.04	2.03±0.10
Clay	14.90	21.10	18.33±1.53
Sand	78.50	78.67	78.56±0.10
Silt	3.00	3.20	3.11±0.10
Control site (n = 16)			
pH	5.40	7.60	6.67±0.57
OM (%)	0.40	0.60	0.50±0.10
Clay	15.00	21.00	17.69±1.53
Sand	80.00	80.33	80.22±0.19
Silt	1.90	2.43	2.09±0.69

Table 2: Heavy metal concentrations in surface soil samples (mg kg^{-1} DW)

Parameters	Min.	Max.	Mean±SD
Study site (n = 16)			
Soil Pb	60.00	143.30	114.79±25.32
Soil Cr	104.20	230.00	181.66±34.79
Soil Cu	58.30	207.50	248.59±212.44
Control site (n = 16)			
Soil Pb	24.33	85.83	59.25±20.02
Soil Cr	33.87	76.23	52.34±14.79
Soil Cu	50.00	84.50	71.15±11.21

Table 3: Correlation matrices between metals in soil of study area

Parameters	Soil Pb	Soil Cr	Soil Cu
Soil Pb	1.000		
Soil Cr	0.374	1.000	
Soil Cu	-0.389	-0.559*	1.000

Table 4: Heavy metal concentrations in pepper samples (mg kg^{-1} DW)

Parameters	Min.	Max.	Mean±SD
Study site (n = 32)			
Plant Pb	11.33	27.00	18.90±4.76
Plant Cr	10.40	35.10	20.04±7.44
Plant Cu	7.56	21.07	14.52±4.23
Metals		Transfer factor (Plant/Soil ratio)	
Pb		0.165	
Cr		0.089	
Cu		0.107	

Table 5: Correlation matrices between metals in pepper sample of study area

Parameters	Plant Pb	Plant Cr	Plant Cu
Plant Pb	1.000		
Plant Cr	0.319	1.000	
Plant Cu	-0.089	0.039	1.000

However, when the levels of these metals in study area were compared with values reported in literature, mean Pb and Cu were found to be higher than 0.046 and 0.439 mg kg^{-1}, respectively reported by Awofolu *et al*. (2005), although below 100 and 100 mg kg^{-1} permissible levels recommended for agricultural soils (Ewers, 1991). Cr was found above the critical permissible concentration of 100 mg kg^{-1} as given by Ewers (1991) and 81.00 mg kg^{-1} reported for agricultural farmland in Addis Ababa (Fisseha, 2002). Generally, the extent of contamination in the farmlands was higher in the study area as compared to standard limits. This might be due to excessive amount of trace metals in the tannery effluents use in irrigation of farmlands. Similar findings were also reported by Moon *et al*. (1991) and Abulkasem and Singh (1999).

Levels Trace Metals in Pepper (*Capsicum annum*) Samples

All pepper samples collected from the farmlands showed the presence of Pb, Cu and Cr. Concentration of Pb, Cu and Cr (mg kg^{-1} DW) is represented on Table 4. From the results, the general trend for the mean levels of metal analysed in pepper samples showed that; Cr > Pb > Cu. As shown on Table 5, positive correlations were revealed between Cr and Pb, Cu and Cr, while negative correlation was showed between Cu and Pb. The positive correlation between metals in soil could indicate similar source of metals. Negative correlation observed among the metals in pepper could indicate different source of these metals.

The results obtained for Pb and Cr in this study are higher than 0.3 mg kg^{-1} recommended by FAO/WHO (2001) and 2.30 mg kg^{-1} recommended for vegetable crops (Weigert, 1991) respectively. While levels of Cu were found lower than 73.3 mg kg^{-1} recommended maximum limits for vegetables

Table 6: Correlation matrices between metals in soil and plant samples of study area

Parameters	Plant Pb	Plant Cr	Plant Cu
Soil Pb	-0.500	-0.332	-0.016
Soil Cr	-0.329	-0.047	0.088
Soil Cu	0.029	-0.433	0.226

Table 7: Correlation matrices of heavy metals and physicochemical parameters of studied soil

Factors	Pb	Cr	Cu
pH	-0.274	0.223	-0.161
OM	-0.274	0.238	-0.250
Clay	-0.222	0.238	-0.151
Sand	-0.962	-0.971	0.987
Silt	0.999	0.859	-0.897

(Weigert, 1991). These findings lead to conclude that the use of effluents for irrigation like Challawa River water is introducing Cr and Pb, which ultimately accumulate in the plants; the practice of using this water could culminate into a health hazard for humans and animals.

Relationships Between the Trace Metals in Pepper and Soils Samples

Pearson's Correlation coefficients between the concentration of trace metals in pepper and in the soils are presented in Table 6. Cu concentration in soil correlated positively with the contents of Pb and Cu in pepper. Also, positive correlation was observed between Cr concentrations in soil with Cu contents in pepper. Negative correlation were found between Pb in soil and with the contents of Pb, Cr and Cu in pepper, Cr in soils and Pb and Cr contents in pepper samples, Cu in soils and with the contents of Cr in pepper samples. The positive relationships among the soil and pepper content metals might be a cause of heavy metals toxicities to plant and animals through their entry into food chain (Abulkasem and Singh, 1999). Negative correlation observed among the soil and plant metals content might be due to soil types, nature of plant, extent and type of industrial effluents etc.

Relationships Between the Physicochemical and Soils Samples

The relationship was also examined for dependency upon some soil factor through the use of correlation analysis (Table 7). pH, Organic Matter (OM), silt fractions, clay fractions correlated positively with Cr indicating that these factors largely control the concentration of this metal in the soils. Negative correlation was found between all physicochemical parameters (except silt fraction for Pb and sand fraction for Cu) and heavy metal (Pb and Cu) concentration in soil.

Transfer Factors for Heavy Metals

As shown on Table 4, the Transfer Factor (TF) of Pb, Cr and Cu from soil to plant, which is one of the key components of human exposure to metals through the food chain. Transfer factors were determined for Pb, Cr and Cu to quantify the relative difference in bioavailability of metals to plants or to identify efficiency of plant specie to accumulate a given metal. These factors were based on the root uptake of metals and discount the foliar absorption of atmospheric metal deposits. Although the degree of accumulation of shows that Pb is more than 2 fold higher than Cr. The reasons could be due to the soil physicochemical properties of soils which may have enhanced soil-plant transfer of metals.

CONCLUSION

The soil on the bank of River Challawa is polluted. This is due to the fact that untreated industrial wastes discharged into the river contaminate it with heavy metals; Pb, Cr and Cu. This has indirectly caused the accumulation of these heavy metals in the agricultural soils through irrigation and subsequently in the pepper planted in them, such that their concentrations in the soils and pepper (except Cu in pepper) exceed the recommended permissible limits. Hence, soil and plant monitoring together with the prevention of metals entering the plant, is a prerequisite in order to prevent potential health hazards of irrigation with River Challawa water.

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