

Assessment of Peppers and Soils for Some Heavy Metals from Irrigated Farmlands on the Bank of River Challawa, Northern Nigeria

U.A. Awode¹, A. Uzairu¹, M.L. Balarabe², G.F.S. Harrisson¹ and O.J. Okunola¹

¹Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria

²Department of Biological Sciences, Ahmadu Bello University, Zaria, Nigeria

Abstract: Assessment of metal-contaminated soils depends on how one can predict the bioavailability of trace and toxic metals in soil and transfer to the human food chain. To predict the uptake of Cd, Zn and Ni by vegetable (pepper) grown on agricultural soil on the bank of river Challawa. 32 pepper and 16 soil samples were collected from areas irrigated with wastewater as study samples and for comparative purposes, agricultural soil samples irrigated with fresh river water, was collected as control samples. The samples were analyzed by flame atomic absorption spectrophotometer. The validation of the sample procedure was assessed by using spiking method. The level of Cd ranged from 0.94-5.27 mg kg⁻¹ and 0.25-1.07 mg kg⁻¹ Dry Weights (DW) for soil and pepper samples respectively. Mean concentration of Zn ranged 123.30-205.00 mg kg⁻¹ and 10.40-35.10 mg kg⁻¹ for samples in similar order as above while that of Ni ranged from 39.30-99.50 mg kg⁻¹ and 2.73-6.90 mg kg⁻¹ also in the same order of samples as mention above. The metals were examined for dependency upon some soil factor through the use of correlation analysis, pH, Organic Matter (OM), sand fractions and clay fractions correlated positively with Cd, Zn and Ni indicating that these factors greatly control the concentration of these metals in the soils. Metal transfer factors from soil to vegetable are found less significant for Cd, Zn and Ni.

Key words: Assessment, heavy metals, pepper, soil

Introduction

Vegetable constitute an important part of the human diet since they contain carbohydrates, proteins, as well as vitamins, minerals and trace elements (Dastane, 1987). However, since recent years their consumption is increasing gradually, particularly among the urban community. This is due to increased awareness on the food value of vegetables, as a result of exposure to other cultures and acquiring proper education (Fisseha, 2002). 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 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, 1995/96).

With the increasing awareness of risk assessment of heavy metal in food crops, monitoring of these metals in pepper is therefore critical as it gives information in nutritional planning and provides data for epidemiological studies (Bruce and Bergstrom, 1983). 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. The aim of this research

is to assess level of heavy metals (Zn, Cd and Ni) in peppers and 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 on irrigated farmland on the bank of River Challawa, Nigeria. 32 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 2mm sieve. 5g of soil samples were placed in 100ml beaker. 3ml 30% hydrogen peroxide was added following a previously described procedure by Shriadah (1999). This was left to stand for 60mins. until the vigorous reaction ceased. 75 mL of 0.5M solution of HCl was added and the content heated gently at low heat on hot plate for about 2 hrs. 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 hrs, 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) was used for digestion of plant sample. 0.5g of sieved samples was then weighed into 100ml beaker. A mixture of 5 mL concentrated Trioxonitrate (IV) acid and 2 mL Perchloric acid was added and this was digested

on low heat using hot plate for 15 minutes at 70°C until a light coloured solution was obtained. The sample solution was not allowed to dry during digestion. The digest was allowed to cool, filtered into 50ml standard flask. The beaker was rinsed with small portions of distilled water and then filters into the flask. Triplicate digestion of each sample was carried out together with blank digest without the 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 multi element metal standard solution (0.5 mgL⁻¹ of Cd and Ni and 5 mgL⁻¹ of Zn). 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 96.6, 90.0 and 97.8% for Cd, Ni and Zn respectively. The recoveries for those of pepper sample were 90.0, 92.8 and 102.2% Cd, Ni and Zn respectively. Recoveries from pepper samples were generally higher than soil samples with Zn 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: Ranges, mean and standard deviation of Cd, Zn and Ni contents in soil of study and control areas are presented in Table 2. Highest concentration of Cd, Zn and Ni 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 and control areas revealed; Zn>Ni>Cd.

Awode et al.: Assessment of Pepper and Soil for Some Heavy Metals

Table 1: Physicochemical Properties of the Soils

	Study Site (n = 16)			
	Min	Max	Mean	(±) SD
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)

	Study Site (n = 16)			
	Min	Max	Mean	(±) SD
Soil Cd	0.94	5.27	2.84	1.48
Soil Zn	123.30	205.00	167.36	26.12
Soil Ni	39.30	99.50	78.80	17.53
Control Site (n = 16)				
Soil Cd	0.27	1.47	1.12	0.28
Soil Zn	32.30	98.50	71.29	17.99
Soil Ni	22.50	49.07	33.23	7.20

Table 3: Correlation Matrices between Metals in Soil of Study Area

	Soil Cd	Soil Zn	Soil Ni
Soil Cd	1.000		
Soil Zn	0.274	1.000	
Soil Ni	-0.095	-0.100	1.000

Table 4: Heavy Metal Concentrations in Pepper Samples (mg kg⁻¹ DW)

	Study Site (n = 16)			
	Min	Max	Mean	(±) SD
Plant Cd	0.25	1.07	0.85	0.21
Plant Zn	10.40	35.10	20.04	7.44
Plant Ni	2.73	6.90	4.66	1.07

Table 5: Correlation Matrices between Metals in Pepper sample of Study Area

	Plant Cd	Plant Zn	Plant Ni
Plant Cd	1.000		
Plant Zn	-0.273	1.000	
plant Ni	0.056	0.075	1.000

Table 6: Correlation Matrices between Metals in Soil and Plant Samples of Study Area

Parameter	Plant Cd	Plant Zn	Plant Ni
Soil Cd	-0.334	0.164	0.238
Soil Zn	-0.007	0.228	-0.204
Soil Ni	-0.599	-0.016	-0.466

As Table 3 show, positive correlation was found between Cd and Zn in soil samples from the study area.

This indicates common source of these metals, which could be related to known geochemical association between the two metals. Negative correlations were found between Ni and Cd, Ni and Zn in soils. This also could indicate different source of these metals in soils of the study area.

However, when the levels of these metals in study area were compared with values reported in literature, mean Cd and Zn were found to be higher than trace levels and 0.3 mg kg⁻¹, respectively reported by Awofolu *et al.* (2005), although below 3 mg kg⁻¹ and 300 mg kg⁻¹ permissible levels for soils recommended by MAFF (1992). Ni was found above the critical permissible concentration of 50 mg kg⁻¹ as given by MAFF (1992) and 74.13 mg kg⁻¹ reported for agricultural farmland in Addis Ababa (Fisseha, 2002). Even though Cd concentrations fall below the critical permissible concentration level, it seems that their persistence loads into the soil through irrigation with waste effluent water from Challawa Industrial Estate might increase over time.

Metal Concentration of Pepper (*Capsicum annum*)

Samples: Ranges, mean and standard deviation of Cd, Zn and Ni concentrations in pepper collected from study area are presented in Table 4. From the results, the general trend for the mean levels of metal analyzed in pepper samples showed that; Zn>Ni>Cd. As shown on Table 5, positive correlations were revealed between Cd and Ni, Zn and Ni, while negative correlation was showed between Cd and Zn. 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 Cd in this study are higher than 0.2 mg kg⁻¹ recommended by FAO/WHO (2001), although lower than 4 mg kg⁻¹ and 1.04 mg kg⁻¹ reported by Chandrappa and Lakeshwari (2006) in a similar studies. Levels of Zn were found lower than 100mgkg⁻¹ recommended for plants (FAO/WHO, 2001). While levels of Ni were found lower than 67.90 mg kg⁻¹ recommended maximum limit for vegetables (Weigert, 1991). However, high level of Cd in the present study could be due to wear and tear of vehicle parts used to convey sand from the river, since this is a common activity along the bank of the River.

Relationships between the heavy metals in pepper and soils samples:

Correlation coefficients between the concentration of heavy metals in pepper and in the soils are presented in Table 6. Cd concentration in soil correlated positively with the contents of Zn and Ni in pepper. Also, positive correlation was observed between Zn concentrations in pepper with its contents in soil.

Awode *et al.*: Assessment of Pepper and Soil for Some Heavy Metals

Table 7: Correlation Matrices of Heavy Metals and Physicochemical Parameters of Studied Soil

Factors	Cd	Zn	Ni
pH	0.970	0.489	0.658
OM	0.970	0.489	0.658
Clay	0.970	0.487	0.658
Sand	0.243	0.872	0.753
Silt	-0.516	-0.977	0.913

Table 8: Transfer factor (TF)

Metals	TF (Plant/Soil ratio)
Pb	0.165
Cr	0.089
Cu	0.107

Negative correlation were found between Cd in pepper and with the contents of Cd, Zn and Ni in soil, Zn in pepper and Ni contents in soil, Ni in pepper and with the contents of Zn and Ni in soils. 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 (Shriadah, 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), sand fractions, clay fractions correlated positively with Cd, Zn and Ni indicating that these factors largely control the concentration of these metals in the soils. Negative correlation was found between silt fractions and heavy metal (Cd and Ni) concentration in soil, although positive correlation was found with Ni.

Transfer factors for heavy metals: Table 8 show the Transfer Factor (TF) of Cd, Zn and Ni 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 Cd, Zn and Ni to quantify the relative difference in bioavailability of metals to plants or to identify efficiency of plant specie to accumulate a given metal. The transfer factors as suggested by Kloke *et al.* (1984) for Cd and Zn (1-10) were used as a generalized range for comparisons. These factors were based on the root uptaken of metals and discount the foliar absorption of atmospheric metal deposits. All samples were below Cd and Zn suggested factor range as suggested by Kloke *et al.* (1984). Although the degree of accumulation of shows that Cd is more than 2 fold higher than Zn. The reasons could be due to the nature of Cd, since Cd is known to be less retained by the soil than other toxin cations (Chandrappa and Lakeshwari, 2006) or the low organic matter contents (Table 1) of soils sampled could have also enhanced soil-plant transfer of metals.

Conclusion: The study concludes that irrigation crops using Challawa river water has increased contamination of Cd and Ni in pepper causing potential health risk in the long term.

References

Agricultural Project Monitoring and Evaluation Unit, Kaduna: Fadama crop production survey and annual reports, 1995/96.

APHA, 1992. Standard Methods for the Examination of Water and Wastewater. 16th Edition. American Public Health Association. New York.

Audu, A.A. and A.O. Lawal, 2005. Variation in Metal Contents of Plants in Vegetable Gardens Sites in Kano Metropolis. *J. Appl. Sci. Environ. Manage.*, 10: 105-109.

Awofolu, O.R., Z. Mbolekwo, V. Mtshemla and O.S. Fotoki, 2005. Levels of Trace Metals in Water and Sediments from Tyume River and its Effects on an Irrigated farmland. *Water S. A.*, 31: 87-94.

Awofolu, O.R., 2005. A survey of Trace metals in vegetation, soil and lower animals along some selected major and Roads in metropolitan city of Lagos. *Environmental monitoring and Assessment*, 105: 431-447.

Bougoucos, G.H., 1951. Determination of Particle Sizes. *Soil Agron. J.*, 43: 434-438.

Bruce, A. and L. Bergstrom, 1983. User requirement for data bases and applications in nutritional research. *Food Nutr. Bull.*, 5: 24-29.

Burton, M.A.S. and P.J. Patterson, 1979. Mineral accumulation by aquatic bryophytes from polluted mined street. *Environ. Pollut.*, 19: 39-45.

Chandrappa, G.T. and H. Lakeshwari, 2006. Impact of Heavy Metal Contamination of Bellandur Lake on Soil and Cultivated Vegetation. *Current Sci.*, pp: 622-627.

FAO/WHO, 2001. Codex Alimentarius Commission. Food additives and contaminants. Joint FAO/WHO Food Standards Programme, ALINORM 01/12A, pp: 1-289.

Das, P., S. Samantaray and G.R. Rout, 1997. Studies on cadmium toxicity in plants: a review, *Environ. Pollut.*, 98: 29-36.

Dastane, N.G., 1987. Use of brackish waters in horticulture. *Water Quality Bull.*, 12: 64-71.

Faruk, O., S. Nazim and S. Metin Kara, 2006. Monitoring of cadmium and micronutrients in spices commonly consumed in Turkey. *Res. J. Agric. Biolo. Sci.*, 2: 223-226.

Fisseha, I., 2002. Metals in leafy vegetables grown in Addis Ababa and toxicological implications. *Ethiop J. Health Dev.*, 16: 295-302.

Herdershot, W.H., H. Lalande and M. Duquette, 1993. Soil reaction and exchangeable acidity. In: Carter, M.R. (Ed), *Soil Sampling and Methods of Analysis for Canadian Society of Soil Science* Lewis, Boca Raton, FL, pp: 141-145.

Awode *et al.*: Assessment of Pepper and Soil for Some Heavy Metals

- Kloke, A., D.R. Sauerbeck and H. Vetter, 1984. The contamination of plants and soils with heavy metals and transport of metals in terrestrial food chain. In 'Changing metal cycles and human health: report of the Dahlem Workshop on Changing Metals Cycles and Human Health, Berlin, Germany'. Ed J.O Nriagu Springer-Verlag: Berlin, pp: 113-141.
- MAFF and Welch Office Agriculture Department, 1992. Code of good agricultural practice for the protection of soil. Draft Consultation Document, MAFF London.
- Shriadah, M.M.A., 1999. Heavy metals in mangrove sediments of the United Arab Emirates shoreline (Arabian Gulf). *Water, Air Soil Pollut.*, 116: 523-534.
- Walkley, A. and I.A. Black, 1934. An examination of the Detjare method for Determining soil organic matter and a proposed modification of the chromic Acid titration. *Soil Sci.*, 37: 29-36.
- Weigert, P., 1991. Metal loads of food of vegetable origin including mushrooms. In: Merian E. Ed. *Metals and their compounds in the environment: occurrence, Analysis and Biological Relevance*. Weinheim: VCH, pp: 458-468.