

**Assessment of health risk associated with heavy metal contamination of edible vegetables in cement contaminated area.**

**Running title:** Cement contamination of edible vegetables around cement factory.

**ABSTRACT**

**Aim:** Heavy metal (HM) content of some vegetables in the vicinity of a cement factory can be a useful index for assessment of HM contamination of the environment associated with cement production.

**Study design:** This cross sectional study was conducted at the United Cement Company at Mfamosing, Akamkpa local government area, Cross River State, Nigeria between February to November 2016.

**Methods:** One hundred and forty edible vegetables of *Telfairia occidentalis* (fluted pumpkin), *Vernonia amygdalina* (bitter leaf), *Amaranthus viriditis* (green leaf), *Talinum triangulare* (water leaf), *Lavantheca africanum*, *Heinsia crinata* and *Gnatum africana* were collected at varying distances and directions from a cement factory site and an area remote to the site serving as control. The lead (Pb), copper (Cu), manganese (Mn), iron (Fe), cadmium (Cd), selenium (Se), chromium (Cr), zinc (Zn) and arsenic (As) content of the vegetable samples were determined using atomic absorption spectrophotometry. Data were analyzed using analysis of variance at  $P = .05$ .

**Results:** The Pb, Cu, Mn, Fe, Cd, Se and Zn content of vegetables in all the locations studied were within the safe limits except for Cr and As levels of some vegetables from location closest to the factory which were higher than the safe limits. The HM content of all vegetables from location closest to the factory were significantly higher than those from other locations ( $P < 0.001$ ). The hazard quotient (HQ) of all HM in all the vegetables were  $< 1$  except for Mn in *T. occidentalis* which was  $> 1$ . The hazard index ( $\Sigma HQ$ ) for all HM in all the vegetables were  $> 1$ .

**Conclusion:** Cement production is associated with chromium and arsenic contamination of edible vegetables and increase in hazard index of HM levels in vegetables closest to the factory which may be implicated in increased risk for development of deleterious health consequences to consumers.

**Key words:** Cement dust, heavy metals, vegetables, contamination

**Word count:** 299

## Introduction

Cement production is one of the major sources of environmental pollution associated with industrialization in developing countries. Cement dust emission has been described as the major source of heavy metal contamination of the environment [1]. Higher values than safe limits have been reported for Pb, Cd, Mn and Cr in water and leafy vegetables in cement contaminated areas [2]. These HM bioaccumulate, enters the food chain with potentials for deleterious impact on the vegetation, animal and human health. In humans, it has been associated with various respiratory, immunologic, hematological diseases, genotoxicity and cancers [3]. In plants, HM toxicity has been associated with inhibitory effect on plants growth, enzymatic activity, stoma functions, photosynthesis and damage to the root system [4]. The intensity and nature of the damage is a function of the concentration of the pollutants and the duration of exposure (dose) while degree of HM accumulation in plants have been shown to be influenced by their relative distance from the metal source and seasonal effects [5].

Vegetables serve as food for man and are the major sources of vitamins and minerals in the diet. HM content of edible vegetables in the vicinity of cement factories **may be used to estimate the level of heavy metal exposure to man** and may be a useful index for monitoring environmental pollution emanating from cement production [6]. To date, information on HM contamination of edible vegetables in the vicinity of united cement factory in Akamkpa, Cross River State Nigeria and associated health risk is still uncertain. Vegetables as *Telfairia occidentalis*, *Vernonia amygdalina*, *Amaranthus viriditis*, *Talinum triangulare*, *Lavandula africanum*, *Heinsia crinata* and *Gnatum africana* constitute the major diet of the population in this locality, therefore knowledge of the HM concentration of these vegetables and monitoring exposures to them through diet may therefore be important in circumventing the health risk associated with their consumption. This study therefore assessed the heavy element content of *Telfairia occidentalis*, *Vernonia amygdalina*, *Amaranthus viriditis*, *Talinum triangulare*, *Lavandula africanum*, *Heinsia crinata* and *Gnatum africana* in the vicinity of the factory to assess the effect of cement dust exposure on the HM content of these vegetables and the potential health risk which may be associated with their consumption.

## Materials and methods

### Study Area.

This study was conducted at the United Cement Company at Mfamosing, Akamkpa local government area, Cross River State, Nigeria. The site is close to 5km west to Mbebi village at coordinate 05.04493°N, 008.298995°E, 5km south to Abifan community at coordinate 05.07591°N, 008.52192°E and 2km east to Mfamosing community and 3km east to main quarry site at coordinate 05.06993°N, 008.53908°E [7].

### Sample collection and preparation

One hundred and forty vegetables samples (4 samples each from each location) comprising of *Telfairia occidentalis* (fluted pumpkin), *Vernonia amygdalina* (bitter leaf), *Amaranthus viriditis* (green leaf), *Talinum triangulare* (water leaf), *Lavandula africanum*, *Heinsia crinata* and *Gnatum africana* were collected from quarry site camp 100m away from cement factory, 3 communities in the vicinity of the factory; Mfanmosing I, 2km east of quarry site (East), Mfanmosing II 3km south of quarry site (South), Mbebi 5km west of quarry site (West), and from Calabar metropolis 45km away from the quarry site (North) which served as the control samples.

Leaves of the vegetable samples were collected in **quadruplet**, wrapped in absorbent paper and taken to the laboratory. Samples were thoroughly washed with distilled water, initially air dried and then oven dried at 70°C to remove all moisture. Dried samples were then crushed using pestle and mortar. Digestion of vegetable samples were done by adding 0.5g of crushed sample into

appropriately labeled chemically clean digestion tubes, followed by the addition of 10ml of Tri-Acid mixture (HNO<sub>3</sub>: HClO<sub>4</sub> and HCl in a ratio of 2:1:2) to obtain a homogenous mixture. Samples were cooled and filtered using Whatman filter paper. The final volume of the filtrate was made up to 50ml with deionised water and then centrifuged at 500g for 5 minutes. The clear supernatant solutions were transferred to a set of plastic vials for the estimation of Pb, Cu, Mn, Fe, Cd, Se, Cr, Zn and As.

## Laboratory methods

### Estimation of heavy metals by Atomic Absorption Spectrophotometry.

Determination of Pb, Cu, Mn, Fe, Cd, Se, Cr, Zn and As was done by atomic absorption spectrophotometer (Model 2380 PerkinElmer Inc., Norwalk, CT, USA) [8].

### Health Risk Assessment

Health risk associated with any pollutant is dependent upon the level of exposure and amount of absorption by human body [9]. Hazard quotient and hazard index have been described as valid tools to assess the level of risk associated with particular pollutant.

### Estimation of hazard quotient (HQ)

An estimate of the potential hazard to human health (HQ) through consumption of vegetables grown in metal-contaminated soil was calculated as described in the equation below [9]:

$$HQ = (Div) \times (C_{metal}) / RfD \times Bo$$

Where (Div) is the daily intake of vegetables (kg per day), (C<sub>metal</sub>) is the concentration of metal in the vegetable (mg kg<sup>-1</sup>). Daily intake of vegetables was taken as 0.100 kg for adults, as this is the minimum vegetable requirement for a balanced diet [10]. Average body weight (Bo) for adults in the study location was 62 kg [11]. Reference oral dose (RfD) (mg/kg/day) for elements studied were Cadmium 0.001 (mg/kg/day), Copper 0.04 (mg/kg/day), Lead 0.004 (mg/kg/day), Iron 0.7 (mg/kg/day) [12], arsenic 0.003 (mg/kg/day), manganese 0.14 (mg/kg/day), zinc 0.3 (mg/kg/day), chromium 1.5 (mg/kg/day) [13], selenium 0.039 (mg/kg/day) [14]. If level of Hazard quotient is less than 1, the risk associated with exposure of metal is negligible. However if level of hazard quotient is higher than 1, the metal may pose serious health hazards [9].

### Estimation of hazard index

The potential risk to human health through more than one metal, the hazard index (HI) has been developed [9]. The hazard index which is the sum of the hazard quotients was calculated as described in equation below:

$$HI = \sum HQ = HQ_{Cd} + HQ_{Fe} + HQ_{Pb} + HQ_{Mn} + HQ_{Cr} + \dots$$

When the hazard index exceeds 1.0, there is concern for potential health effects [15].

### Statistical analysis

Data analysis was done using the statistical package for social sciences (SPSS version 20.0). Analysis of variance (ANOVA) was used to test significance of variations within and among group means and Fisher's least significant difference (LSD) post hoc test was used for comparison of multiple group means. A probability value  $p < 0.05$  was considered statistically significant.

## RESULTS

The essential metal (Mn, Fe, Zn, Cu, Se) content of vegetables in all the locations studied were shown in table 1. The mean concentration of the essential metal in all the vegetables studied varied significantly with the vegetable type and the location of the vegetable from the cement factory ( $p < 0.001$ ). The essential metal content of the vegetable sample collected from all locations was within the recommended safe limits for these metals in vegetable samples.

Table 2 shows non-essential metal (Pb, Cr, As, Cd) content of edible vegetables in all the locations studied. The edible vegetable content of non-essential metal studied varied significantly with the vegetable type and the location of the vegetable from the cement factory ( $p < 0.001$ ). The non-essential metal content of the vegetable sample collected from all locations were within the recommended safe limits for these metals in vegetable samples except for Cr and As levels of some vegetables from Camp closest to the cement factory plant which were observed to be higher than the safe limits.

The comparison of all metals (essential and non-essential) in all vegetable samples from camp against other locations using post hoc analysis was depicted in table 3. Significantly higher levels of Mn, Fe, Zn, Se and Cd were observed in vegetables samples from Camp closest to the cement plant than those from other locations ( $p < 0.001$ ). Edible vegetables from Camp had higher Cr and Cu levels compared to East, South and North (control) ( $p < 0.001$ ).

The comparison of all metals (essential and non-essential) in all vegetable samples from North (control) against other locations using post hoc analysis was depicted in table 4. Significantly higher levels of Cu, Fe, Mn and lower levels of Cr and As were observed in vegetables samples from North (control) compared to those from other locations ( $p < 0.001$ ). Edible vegetables from west had higher Cr and As levels compared to those from east ( $p < 0.001$ ).

The calculated hazard quotient (HQ) and hazard index (HI) of the metals in different vegetables studied was shown in table 5. The calculated HQ of all the heavy metals in all the vegetables studied were below 1 except for Mn in *Telfaria occidentalis* whose HQ is greater than 1. The calculated HI ( $\Sigma$ HQ) of all the elements in all the vegetables studied was above 1 indicating potential risk to human health via consumption of these vegetables.

**Table 1: Essential metal content of vegetable samples from Camp, West, East and South of Camp and North (control)**

| HM<br>(mg/kg) | Location | Amaranthus<br>Viriditis | Talinum<br>Triangulare | Vernonia<br>Amygdalina | Telfaria<br>Occidentalis | Lavantheca<br>Africanum | Heinsia<br>Crinata | Gnatum<br>Africana | Location<br>Effect<br>F | p     | Vegetable Effect<br>F | p     | Loc/Veg<br>Effect<br>F | p     | Safe<br>limit |
|---------------|----------|-------------------------|------------------------|------------------------|--------------------------|-------------------------|--------------------|--------------------|-------------------------|-------|-----------------------|-------|------------------------|-------|---------------|
| Mn            | Camp     | 84.23±0.93              | 62.38±0.71             | 96.65±0.85             | 104.83±1.39              | 87.71±0.54              | 79.59±0.73         | 48.62±2.43         | 136.87                  | <.001 | 275.03                | <.001 | 19.49                  | <.001 | 500 [16]      |
|               | West     | 62.11±3.22              | 59.272±1.2             | 60.60±0.40             | 75.36±0.494              | 67.77±0.68              | 64.11±4.55         | 58.41±0.52         |                         |       |                       |       |                        |       |               |
|               | East     | 59.29±4.69              | 53.86±1.22             | 55.33±0.87             | 68.781±0.72              | 76.36±5.26              | 44.82±0.97         | 54.56±1.13         |                         |       |                       |       |                        |       |               |
|               | South    | 46.02±1.33              | 48.48±1.57             | 54.35±1.08             | 62.66±0.989              | 73.67±2.73              | 55.22±0.99         | 55.22±0.99         |                         |       |                       |       |                        |       |               |
|               | North    | 59.53±2.62              | 59.34±0.49             | 49.57±0.74             | 90.661±4.22              | 63.44±0.56              | 68.60±0.97         | 66.07±0.76         |                         |       |                       |       |                        |       |               |
| Fe            | Camp     | 122.45±1.4              | 139.16±1.2             | 160.17±0.6             | 149.70±0.61              | 145.83±0.9              | 158.74±0.5         | 145.21±0.82        | 358.71                  | <.001 | 18.00                 | <.001 | 21.69                  | <.001 | 425 [16]      |
|               | West     | 74.56±1.77              | 70.70±1.28             | 89.48±0.39             | 86.44±0.79               | 84.47±0.94              | 89.23±0.72         | 75.39±0.74         |                         |       |                       |       |                        |       |               |
|               | East     | 70.30±2.34              | 80.36±1.24             | 62.75±0.53             | 50.30±0.49               | 65.66±1.28              | 58.40±2.23         | 60.20±0.89         |                         |       |                       |       |                        |       |               |
|               | South    | 88.28±0.45              | 70.66±0.70             | 92.61±0.79             | 82.41±0.23               | 83.22±0.78              | 77.38±1.21         | 84.07±1.02         |                         |       |                       |       |                        |       |               |
|               | North    | 69.84±2.35              | 85.73±0.47             | 86.52±0.70             | 82.63±0.92               | 38.62±0.59              | 63.61±1.22         | 80.73±0.74         |                         |       |                       |       |                        |       |               |
| Zn            | Camp     | 31.73±0.65              | 30.18±1.40             | 36.02±0.87             | 52.65±0.60               | 24.52±1.19              | 33.66±0.57         | 40.41±0.52         | 321.99                  | <.001 | 264.2                 | <.001 | 36.35                  | <.001 | 60 [17]       |
|               | West     | 13.80±2.55              | 12.28±0.69             | 10.59±0.72             | 38.93±0.14               | 21.23±0.76              | 16.32±0.97         | 20.41±0.73         |                         |       |                       |       |                        |       |               |
|               | East     | 27.35±1.13              | 16.10±1.25             | 11.57±0.86             | 39.25±0.73               | 25.24±0.91              | 19.12±1.33         | 18.14±0.76         |                         |       |                       |       |                        |       |               |
|               | South    | 14.35±1.12              | 12.35±1.21             | 15.67±0.72             | 13.89±0.96               | 14.56±0.88              | 11.84±0.70         | 12.74±1.62         |                         |       |                       |       |                        |       |               |
|               | North    | 9.46±0.56               | 14.59±0.86             | 10.40±0.97             | 15.71±0.46               | 23.54±1.31              | 12.49±0.98         | 26.29±0.55         |                         |       |                       |       |                        |       |               |
| Cu            | Camp     | 11.98±1.21              | 16.22±1.02             | 13.62±0.91             | 29.56±0.89               | 17.99±0.11              | 14.73±0.89         | 18.65±0.61         | 4.23                    | .003  | 51.03                 | <.001 | 13.68                  | <.001 | 40 [18]       |
|               | West     | 18.57±1.46              | 9.75±0.72              | 10.71±1.14             | 23.82±0.64               | 28.25±0.89              | 16.27±0.74         | 20.54±0.47         |                         |       |                       |       |                        |       |               |
|               | East     | 12.96±0.83              | 12.86±0.73             | 13.69±0.64             | 12.36±0.53               | 13.16±1.33              | 12.86±1.03         | 14.15±0.77         |                         |       |                       |       |                        |       |               |
|               | South    | 10.12±0.56              | 11.60±1.05             | 9.52±0.16              | 9.98±1.64                | 10.92±0.88              | 11.35±1.01         | 9.21±1.46          |                         |       |                       |       |                        |       |               |
|               | North    | 19.66±1.02              | 19.15±1.49             | 14.52±0.69             | 13.72±0.88               | 12.57±1.23              | 14.77±0.86         | 28.44±0.89         |                         |       |                       |       |                        |       |               |
| Se            | Camp     | 0.030±0.002             | 0.029±0.002            | 0.042±0.002            | 0.032±0.001              | 0.038±0.001             | 0.030±0.001        | 0.036±0.004        | 236.96                  | <.001 | 10.30                 | <.001 | 16.17                  | <.001 | 0.1[19]       |
|               | West     | 0.009±0.001             | 0.007±0.001            | 0.014±0.001            | 0.010±0.000              | 0.006±0.001             | 0.014±0.001        | 0.018±0.001        |                         |       |                       |       |                        |       |               |
|               | East     | 0.011±0.001             | 0.007±0.001            | 0.014±0.001            | 0.019±0.001              | 0.013±0.029             | 0.013±0.101        | 0.012±0.041        |                         |       |                       |       |                        |       |               |
|               | South    | 0.010±0.066             | 0.013±0.001            | 0.013±0.002            | 0.011±0.071              | 0.010±0.221             | 0.012±0.001        | 0.011±0.054        |                         |       |                       |       |                        |       |               |
|               | North    | 0.013±0.001             | 0.014±0.002            | 0.013±0.001            | 0.008±0.001              | 0.010±0.001             | 0.012±0.001        | 0.005±0.001        |                         |       |                       |       |                        |       |               |

Loc = location, Vege = vegetable

**Table: 2: Non-essential metal content of vegetable samples from Camp, West, East and South of Camp and North (control).**

| Element (mg/kg) | Location | Amaranthus Viriditis | Talinum Triangulare | Vernonia Amygdalina | Telfaria Occidentalis | Lavandula stoechas | Heinsia Crinata | Gnathochloa Africana | Location Effect F | Location Effect p | Vegetable Effect F | Vegetable Effect p | Location/Vegetable Effect F | Location/Vegetable Effect p | Safe Limit |
|-----------------|----------|----------------------|---------------------|---------------------|-----------------------|--------------------|-----------------|----------------------|-------------------|-------------------|--------------------|--------------------|-----------------------------|-----------------------------|------------|
| Pb              | Camp     | 0.073±0.02           | 0.04±0.001          | 0.04±0.002          | 0.028±0.001           | 0.03±0.001         | 0.029±0.001     | 0.031±0.002          |                   |                   |                    |                    |                             |                             | 0.3 [16]   |
|                 | West     | 0.037±0.002          | 0.046±0.001         | 0.051±0.001         | 0.044±0.002           | 0.053±0.002        | 0.026±0.001     | 0.039±0.001          |                   |                   |                    |                    |                             |                             |            |
|                 | East     | 0.045±0.014          | 0.044±0.008         | 0.047±0.001         | 0.039±0.001           | 0.042±0.022        | 0.044±0.026     | 0.041±0.010          | 5.09              | 0.001             | 10.52              | <.001              | 10.58                       | <.001                       |            |
|                 | South    | 0.044±0.016          | 0.037±0.002         | 0.047±0.002         | 0.044±0.003           | 0.042±0.002        | 0.041±0.010     | 0.040±0.012          |                   |                   |                    |                    |                             |                             |            |
|                 | North    | 0.029±0.001          | 0.058±0.002         | 0.033±0.001         | 0.037±0.001           | 0.029±0.001        | 0.035±0.001     | 0.037±0.001          |                   |                   |                    |                    |                             |                             |            |
| Cr              | Camp     | *2.937±0.101         | *2.591±0.73         | *3.221±0.21         | *3.050±0.127          | *3.334±0.12        | *3.161±0.097    | *2.964±0.09          |                   |                   |                    |                    |                             |                             | 2.3[16]    |
|                 | West     | 1.698±0.696          | 1.740±0.147         | 1.835±0.079         | 1.928±0.077           | 2.106±0.126        | 2.266±0.112     | 2.44±0.09            |                   |                   |                    |                    |                             |                             |            |
|                 | East     | 1.927±0.102          | 2.299±0.835         | 2.742±0.523         | 2.027±0.100           | 2.222±0.056        | 2.134±0.064     | 2.124±0.001          | 17.10             | <.001             | .526               | .787               | 3.34                        | <.001                       |            |
|                 | South    | 3.071±0.149          | 2.272±0.995         | 2.371±0.149         | 3.424±0.109           | 3.461±0.124        | 1.780±0.051     | 3.562±0.098          |                   |                   |                    |                    |                             |                             |            |
|                 | North    | 1.95±1.261           | 1.938±0.148         | 1.81±0.054          | 1.966±0.068           | 1.759±0.084        | 1.556±0.159     | 1.935±0.047          |                   |                   |                    |                    |                             |                             |            |
| As              | Camp     | *0.221±0.011         | 0.190±0.002         | *0.225±0.02         | 0.198±0.007           | *0.223±0.10        | 0.195±0.011     | 0.198±0.008          |                   |                   |                    |                    |                             |                             | 0.2 [17]   |
|                 | West     | 0.167±0.038          | 0.138±0.009         | 0.164±0.005         | 0.145±0.006           | 0.181±0.010        | 0.199±0.007     | 0.186±0.009          |                   |                   |                    |                    |                             |                             |            |
|                 | East     | 0.194±0.021          | 0.192±0.017         | 0.197±0.007         | 0.198±0.007           | 0.195±0.144        | 0.193±0.026     | 0.190±0.042          | 11.40             | <.001             | 6.99               | <.001              | 7.41                        | <.001                       |            |
|                 | South    | 0.192±0.221          | 0.174±0.013         | 0.155±0.002         | 0.184±0.008           | 0.176±0.034        | 0.182±0.011     | 0.186±0.102          |                   |                   |                    |                    |                             |                             |            |
|                 | North    | 0.185±0.025          | 0.141±0.007         | 0.185±0.006         | 0.134±0.005           | 0.183±0.007        | 0.174±0.008     | 0.130±0.006          |                   |                   |                    |                    |                             |                             |            |
| Cd              | Camp     | 0.026±0.001          | 0.006±0.001         | 0.048±0.011         | 0.038±0.001           | 0.028±0.001        | 0.038±0.001     | 0.046±0.002          |                   |                   |                    |                    |                             |                             | 0.1[16]    |
|                 | West     | 0.008±0.001          | 0.006±0.001         | 0.009±0.001         | 0.007±0.001           | 0.005±0.001        | 0.002±0.001     | 0.007±0.001          |                   |                   |                    |                    |                             |                             |            |
|                 | East     | 0.002±0.004          | 0.002±0.002         | 0.002±0.001         | 0.002±0.001           | 0.002±0.006        | 0.021±0.001     | 0.019±0.001          | 393.7             | <.001             | 32.63              | <.001              | 37.10                       | <.001                       |            |
|                 | South    | 0.008±0.034          | 0.007±0.044         | 0.007±0.002         | 0.008±0.002           | 0.008±0.042        | 0.006±0.001     | 0.007±0.022          |                   |                   |                    |                    |                             |                             |            |
|                 | North    | 0.002±0.001          | 0.002±0.001         | 0.004±0.001         | 0.002±0.001           | 0.001±0.000        | 0.002±0.001     | 0.002±0.001          |                   |                   |                    |                    |                             |                             |            |

\* = above safe limits

**Table 3: Comparison of all metal levels in all vegetable samples from Camp, West, East and South of Camp and North (control) using post hoc analysis.**

| Locations  | Elements<br>(mg/kg) | Mean difference | F-value | p-value |
|------------|---------------------|-----------------|---------|---------|
| Camp/West  | Mn                  | 22.124±3.080    | 24.325  | <0.001  |
|            | Fe                  | 65.280±2.867    | 216.382 | <0.001  |
|            | Zn                  | 15.222±1.945    | 27.640  | <0.001  |
|            | Se                  | 0.022±0.001     | 175.176 | <0.001  |
|            | Cd                  | 0.025±0.002     | 98.119  | <0.001  |
| Camp/East  | Mn                  | 19.006±4.063    | 24.325  | <0.001  |
|            | Fe                  | 81.978±3.783    | 216.382 | <0.001  |
|            | Zn                  | 12.202±2.566    | 27.640  | <0.001  |
|            | Cr                  | 1.062±0.170     | 25.775  | <0.001  |
|            | As                  | 0.034±0.011     | 16.181  | 0.024   |
|            | Se                  | 0.020±0.001     | 175.176 | <0.001  |
|            | Cd                  | 0.029±0.002     | 98.119  | <0.001  |
| Camp/South | Mn                  | 37.074±4.063    | 24.325  | <0.001  |
|            | Fe                  | 66.231±3.783    | 216.382 | <0.001  |
|            | Zn                  | 21.222±2.566    | 27.640  | <0.001  |
|            | Cu                  | 6.433±1.683     | 9.004   | 0.002   |
|            | As                  | 0.040±0.011     | 16.181  | 0.004   |
|            | Se                  | 0.021±0.001     | 175.176 | <0.001  |
|            | Cd                  | 0.024±0.002     | 98.119  | <0.001  |
| Camp/North | Mn                  | 17.247±3.115    | 24.325  | <0.001  |
|            | Fe                  | 73.272±2.900    | 216.382 | <0.001  |
|            | Zn                  | 17.635±1.967    | 27.640  | <0.001  |
|            | Cr                  | 1.071±0.130     | 25.775  | <0.001  |
|            | As                  | 0.039±0.009     | 16.181  | <0.001  |
|            | Se                  | 0.024±0.001     | 175.176 | <0.001  |
|            | Cd                  | 0.029±0.001     | 98.119  | <0.001  |

**Table 4: Comparison of all metal levels in all vegetable samples from Camp, West, East and South of Camp with North (control) using post hoc analysis.**

| Locations   | Parameter (ppm) | Mean difference | F-value | p-value |
|-------------|-----------------|-----------------|---------|---------|
| North/West  | Fe              | 7.992±2.738     | 216.382 | 0.033   |
|             | Cr              | -0.873±0.123    | 25.775  | <0.001  |
|             | As              | -0.036±0.008    | 16.181  | <0.001  |
| North/East  | Cu              | 5.435±1.640     | 9.004   | 0.010   |
| North/South | Mn              | 19.827±3.959    | 24.325  | <0.001  |
|             | Cu              | 7.583±1.640     | 9.004   | <0.001  |
|             | Cr              | -0.890±0.165    | 25.775  | <0.001  |
|             | As              | -0.079±0.011    | 16.181  | <0.001  |
| West/ East  | Fe              | 16.698±3.660    | 216.382 | <0.001  |
|             | Cu              | 5.969±1.629     | 9.004   | 0.003   |
|             | Cr              | -0.864±0.164    | 25.775  | <0.001  |
|             | As              | -0.031±0.011    | 16.181  | 0.035   |
| West/ South | Mn              | 14.950±3.931    | 24.325  | 0.002   |
|             | Cu              | 8.117±1.629     | 9.004   | <0.001  |
|             | As              | 0.042±0.011     | 16.181  | 0.001   |
| East/South  | Mn              | 18.068±4.741    | 24.325  | 0.002   |
|             | Fe              | 15.747±4.414    | 216.382 | 0.004   |
|             | Zn              | 9.021±2.994     | 27.640  | 0.025   |
|             | Cr              | 0.882±0.198     | 25.775  | <0.001  |
|             | As              | 0.074±0.013     | 16.181  | <0.001  |



**Table 5: Hazard quotients (HQ) and Hazzard Index (HI) of all metals in different Vegetables studied**

| Element<br>(mg/kg) | <i>Amaranthus<br/>Viriditis</i> | <i>Talinum<br/>Triangulare</i> | <i>Vernonia<br/>Amygdalina</i> | <i>Telfaria<br/>Occidentalis</i> | <i>Lavanthea<br/>Africanum</i> | <i>Heinsia<br/>Crinata</i> | <i>Gnatum<br/>Africana</i> |
|--------------------|---------------------------------|--------------------------------|--------------------------------|----------------------------------|--------------------------------|----------------------------|----------------------------|
| Mn                 | 0.86                            | 0.65                           | 0.75                           | 1.11*                            | 0.85                           | 0.71                       | 0.72                       |
| Fe                 | 0.0096                          | 0.0092                         | 0.011                          | 0.0099                           | 0.0099                         | 0.010                      | 0.0084                     |
| Zn                 | 0.098                           | 0.092                          | 0.095                          | 0.20                             | 0.12                           | 0.10                       | 0.13                       |
| Cu                 | 0.67                            | 0.56                           | 0.50                           | 0.80                             | 0.83                           | 0.58                       | 0.99                       |
| Pb                 | 0.019                           | 0.018                          | 0.017                          | 0.015                            | 0.016                          | 0.013                      | 0.015                      |
| Cr                 | 0.0025                          | 0.0025                         | 0.0026                         | 0.0027                           | 0.0025                         | 0.0027                     | 0.0029                     |
| As                 | 0.95                            | 0.85                           | 0.80                           | 0.85                             | 0.97                           | 0.94                       | 0.96                       |
| Se                 | 0.0007                          | 0.00057                        | 0.00083                        | 0.0007                           | 0.0007                         | 0.0007                     | 0.0005                     |
| Cd                 | 0.019                           | 0.008                          | 0.024                          | 0.019                            | 0.019                          | 0.019                      | 0.008                      |
| HI( $\Sigma$ HQ)   | 2.63                            | 2.19                           | 2.20                           | 3.01                             | 2.82                           | 2.38                       | 2.83                       |

\* = may pose serious health risk

## DISCUSSION

Cement production results in neighbourhood pollution and deposition of cement dust on the vegetation, topmost soil and water bodies in the vicinity of the cement plant leading to changes in both physical and chemical characteristics of the natural environment/ecosystem. The degree of deposition and deleterious consequences is a function of relative distances from the cement plant. The HM contamination of some edible vegetables samples collected at various distances from a cement factory site was determined in this study.

In this study, the Mn, Fe, Zn, Cu, Se, Pb, and Cd content of vegetables in all the locations studied were below the recommended safe limits for vegetables. Contrary to our findings Zn, Cu and Pb content of the vegetables around Ewekoro cement factories were reported to be above permissible levels for both the soils and the plants samples [20]. However, the Cr and As levels of some vegetables at location closest to the factory (camp) was observed to be higher than the recommended safe limit (for Cr  $2.937 \pm 0.101$ ,  $2.591 \pm 0.73$ ,  $3.221 \pm 0.21$ ,  $3.050 \pm 0.127$ ,  $3.334 \pm 0.12$ ,  $3.161 \pm 0.097$ ,  $2.964 \pm 0.09$  versus 2.3 safe limit set by joint FAO/WHO, 2001; for As  $0.221 \pm 0.011$ ,  $0.225 \pm 0.02$ ,  $0.223 \pm 0.10$  versus 0.2 safe limit [17]). The Cr and As levels in vegetables from the reference or control environment (North) was found to be within the safe limit. Higher values than safe limits have also been observed for Cd and Cr in leafy vegetable especially Spinach, in cement contaminated areas [21]. The proximity of this location to the cement plant may be responsible for the Cr and As contamination of these vegetables rather than from other contamination sources. Prolonged consumption of HM through food stuff beyond maximum permissible level (MPL) has been shown to result in their accumulation on vital organs leading to nervous, cardiovascular, hepatic, renal, neurological impairment as well as bone diseases and several other health disorders [22].

The mean concentration of the elements in all the vegetables studied varied with the vegetable type and the location of the vegetable from the cement factory. Variations in the concentrations of HM in vegetables have been ascribed to the concentration of HM of their production sites, the vegetable type, difference in uptake capabilities and their translocation to the edible portion of the plants [23]. The uptake, accumulation and translocation of HM in plants may vary in different species due to anatomical and physiological differences [24]. Differences in the nature and structure of the plant leaves may be responsible for the differences in the concentrations of trace metals in the foliar part even for those collected from the same area. Hairy and waxy leaves retain more HM compared to leaves without hairs or wax. The wax and hairs present on the surface of these leaves traps the HM deposits on their surface thereby increasing their retention and absorption by these leaves unlike leaves with smooth surfaces [2]. Foliar absorption of solutes also depend on the plant species its nutritional status, the thickness of its cuticle, the age of the leaf, the presence of the stomata guard cells, the humidity of the leaf surface and the nature of the solutes [25]. Certain species of plants have been found to accumulate very high concentration of certain HM and these are referred to as hyper accumulator species [26]. Because of these properties, plant leaves are used as bioindicators and/or biomonitors of HM pollution. The amount of metal in the leaf tissues of herbaceous and woody plant species growing near emission sources reflects the pollution level of these areas [2].

The mean HM content of all the vegetables from camp closest to the cement plant were significantly higher than those from other locations studied. This observation implies that higher metal content of vegetables in this location may be the result of contamination of these vegetables by cement dust emanating from the cement factory. Analysis of vegetables grown in locations close to industries has reported elevated levels of heavy metals contaminants [2, 27]. Cement dust generated during cement production is dispersed into the

atmosphere in form of aerosols and particulate matter. These aerosols can be deposited on soil and are absorbed by vegetables, or alternatively deposited on leaves and fruits and then absorbed. The uptake and bioaccumulation of HM in vegetables are influenced by a number of factors such as climate, atmospheric depositions, the concentrations of HM in soil, the nature of soil on which the vegetables are grown and the degree of maturity of the plants at the time of harvest [27]. Field studies have found positive relationships between atmospheric metal deposition and elevated concentrations of HM in plants and top soil. Elevated levels of some HM as Pb, Ni, Cr, Zn, Cd, and Cu have been reported in vegetable samples in the vicinity of cement factory sites [2, 24].

The calculated HQ of all the metals in all the vegetables studied were below 1 except for Mn in *Telfaria Occidentalis* whose HQ is greater than 1. This indicates that the metal content of these vegetables is safe with no risk to human health. Bio-accumulation of Mn has also been described in some plants grown around cement factories [20]. The reason for slightly higher HQ for Mn in *Telfaria Occidentalis* (1.11 compared to <1.0) is not known but may be related to the higher daily intake since this vegetable is the most consumed on daily basis in the population studied. Higher HQ value for Mn implies that Mn though vital for human life can cause severe toxicity symptoms when in excess. Mn toxicity in animals has been linked with depressed growth, appetite and altered brain function [28]. However, the Mn content of the other vegetables was below the recommended safe limit.

The calculated HI of all the metals in all the vegetables studied was above 1 indicating potential risk to human health via consumption of these vegetables. The hazard index which is the sum of all the hazard quotients put together, assumes that the magnitude of the adverse effect will be proportional to the sum of multiple metal exposures [15]. Even though there was no apparent risk when each metal was analyzed individually, the potential risk could be multiplied when considering all HMs. This implies that excessive consumption of these edible vegetables should be discouraged to avert health risk that may be associated with cumulative exposure. Vegetables are essential component of human diet and some metals present in vegetables are important biochemically and physiologically for health [22], while some HM like mercury, As, Pb, Cd and Cr (VI) are toxic depending on the dose [29]. The consumption of HM contaminated food can seriously deplete some essential nutrients in the body that can lead to decreased immune function, intrauterine growth retardation, impaired psycho-social facilities, disabilities associated with malnutrition and increased risk for cancers [28, 30].

## Conclusion

The findings of this study have shown that edible vegetables cultivated at locations closest to the cement factory studied have higher HM content though within the permissible limit and therefore poses no risk to human health except for their Cr and As content which are slightly above the safe limit with potentials for organ and systemic toxicities. However, long term consumption of these vegetables may result in chronic cumulative effects and undesirable health consequences. Proper assessment of the degree of risk posed by consumption of these vegetables is necessary in order to implement appropriate remediation strategies to avert undesirable health concerns.

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