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Assessment of Heavy Metal Content in Some Selected Agricultural Products Planted Along Some Roads in Nasarawa State, Nigeria

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Abstract: The levels of iron (Fe), zinc (Zn), copper (Cu), manganese (Mn), lead (Pb), cadmium (Cd) and mercury (Hg) content were determined in samples of maize, (*Zea mays*) guinea corn (*Sorghum bicolor*), bambara groundnut (*Vigna subterranean*) and cowpea (*Vigna unguiculata*) obtained in six different locations along some roads within Nasarawa State, Nigeria by flame atomic absorption spectrophotometery in order to assess the effect of accumulation of the metals of interest on crops as a measure of environmental pollution. The mineral mean value for different locations ranged between: Fe (1.6-18.0, 0.75-7.0; 1.0-29.0 and 2.0-20.0), Zn (2.5-3.1; 2.0-10.2. 0 and 1. 0- 4.0), Cu (0.32-0.42; 0.6-2.0; 1.0-7.0 and 0.48-3.5), Mn (0.03-0.56; 0.31-2.0; 0.5-22 and 0.6-4.5), Pb (0.35-1.35; 1.0-2.1; 1.0-44.0 and 3.2-15.1), Cd (0.15-0.22; 0.15-0.9; 1.0-2.0 and 0.5-1.0) and Hg (not available; 0.1-0.3; 1.0-1.2 and 0.2-1.2) mg/100 g samples of maize, guinea corn, bambara groundnut and cowpea, respectively. The results showed that exhaust gas being released from the automobiles can contribute to the level of lead present in crops and the studied crops can contribute significant amount of cadmium toxicity in diet.

Key words: Agricultural products, heavy metal content, atomic absorption spectrophotometer

INTRODUCTION

Some of the natural components of the earth crust are heavy metals. Since they cannot be degraded or destroyed to a small extent, they enter our bodies via food chain, drinking water and air[1]. Zinc (Zn), copper (Cu), chromium (Cr), nickel (Ni), lead (Pb), cadmium (Cd) are examples of heavy metals. Heavy metals produce their toxicity by forming complexes or ligands with organic compounds and active sites of enzymes. At high concentrations, they are dangerous because they tend to bioaccumulate. Heavy metals are accumulated in living things than they are broken down[2,3] of the non-essential heavy metals, most attention is currently paid to lead, mercury and cadmium because they pose the greatest risk to human health from environmental restriction on the use of these elements as new research reveals that they may be causing neurological damage to the unborn babies and young children[4].

Lead is a common industrial metal that has become widespread in air, water, soil and food. It is a naturally occurring element that has been used almost since the beginning of civilization. As a result of the many industrial activities that have brought about its wide distribution. Lead is ubiquitous in the environment today. Two co-workers[5] have compiled a list of 120 occupations (e.g. automechanic, painting, printing and welding) that may involve exposure to lead. It has been reported that the body level of modern humans are about 500 times higher than those of pre-industrial time. Through lead poisoning is cumulative, it causes physiological and neurological disorders such as stillbirth, abdominal pains and anaemia[6,7]. Neurotonic effect of lead includes reduction in nerve conduction and inflammation of the brain[8].

Mercury is an important industrial material for example in the chloroalkali industry and in the manufacture of small batteries[9]. The toxic effects of mercury on physiological and neurological systems of the body have been well characterized[10,11].

Cadmium like mercury is an industrially important metal which is used directly in electroplating and also found in processes associated with zinc and phosphorus. Cadmium derives its toxicological similarity to zinc, an essential micronutrient for plants, animals and humans. In humans long term exposure to cadmium is associated with renal dysfunction. High exposure can lead to obstructive lung disease and has been likened to lung cancer, bone defects, osteomalaria, osteoporosis in humans and animals[12].

One of the ways that metals are released into the environment is by human activity such as agriculture,

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mining, industrial discharge, combustion of leaded fuel, etc. Organic lead compounds (tetraethyl lead and tetramethyllead) are extensively used as additives in petrol. Africa's contribution to global lead pollution has increased from just 5% in the 1980s to 20% in 1996[13-16]. It was also reported that the main source of human adult exposure in Nigeria are food, accounting for over 60% of blood levels, air inhalation, accounting for approximately 30% and water, 10%[17]. Some reported works have shown that planted crops and vegetations along major roads where there was high traffic volume contained high levels of lead content due to automobile exhaust[18-20]. In this study heavy metals in maize, guinea corn, bambara groundnut and cowpea planted along some roads within Nasarawa State, Nigeria were determined in order to assess the effect of accumulation as a measure of environmental pollution. The crops were selected because they are of most widely distributed of Nasarawa State food plants. Their position hold special positions in the agriculture of the state.

MATERIALS AND METHODS

Sampling: Samples of the Agricultural products were connected at different times during harvest period in 2005, directly from the farmers at six different locations along high ways and rural roads within Nasarawa state, Nigeria. The sample seeds collected were maize (*Zea mays*), guinea corn (*Sorghum bicolor*), bambara groundnut (*Vigna subterranean*) and cowpea (*Vigna unguiculata*). Name of roads according to Township/Village linkage (as appropriate) were used in the various Table. Sample seeds collected from different location were of the same varieties.

Sample treatment and analysis: The seeds were thoroughly screened to remove the bad ones and the remaining good ones were dry milled into flour, stored in a polyethylene bags and kept in refrigerator at 40°C until used. Dry ashing of the seed flour was done at 550°C using muffle furnace. The ash obtained was boiled with 15 cm^3 of 20% hydrochloric acid in a beaker, filtered into a 100 cm^3 standard flask and made up to mark with distilled water. The resulting solutions were then analysed for trace heavy metals by Flame Atomic Absorption Spectrophotometer (FAAS) using Alpha 4 model[21] Appropriate weighing was done using Metler Balance.

Statistical analysis: Data obtained were subjected to statistical evaluation. Parameters evaluated were range, standard deviation and coefficient of variation percent[22].

RESULTS AND DISCUSSION

Table 1 shows the moisture, ash and heavy metal content of maize samples. The obtained mean values for moisture and ash content are in excellent agreement with those reported by some workers[18,23,24]. Iron was the most concentrated of the heavy metals with value of 18.0±0.2 mg/100 g sample in Nasarawa-Ugede road while manganese was the lowest (0.03±0.1 mg/100 g sample) in Keffi-Abuja road. The iron content in Nasarawa-Ugede road is too high when compared with those in other chosen producing areas, the reason may be due to the level of mineral in the soil where the maize was grown more so that Ugede/Mbeki in Nasarawa State is well known for mineral resources. Mercury was not detected in any of the locations so also lead was not detected in Keffi-Nasarawa, Nasarawa-Ugede and Keffi-Kanfancha roads. The same parameters are also shown in Table 2 for guinea corn sample. Moisture and ash content with range values of 5.8-6.5 and 3.8-4.3 mg/100 g sample and CV% of 6.6 and 4.3, respectively showing that they were evenly distributed among the samples from different locations. The most high concentrated heavy metals was zinc (10.2±0.1 mg/100 g) found in Akwanga-Lafia road while the lowest was mercury (0.1±0.1 mg/100 g sample) which was also found in Akwanga-Lafia road. Lead, cadmium are mercury were not detected in some locations.

Table 3 shows the results of bambara groundnut sample. Moisture and ash content in this report were in sharp contrast with the values of 2.1 and 4.3%, respectively reported by Aremu *et al*[25]. The reason may be due to the different in drying rate and heavy metal content of the sample. However, the values compare favourably within samples in different locations with CV% of 10.6 and 10.5. Iron content mean value of 29.0±0.1 mg/100 g sample was highly concentrated in Nasarawa-Ugede road while the lowest was manganese (0.5±0.1 mg/100 g) in Keffi-Kanfanchan road. Cadmium and mercury were not detected in some locations. Results of that of cowpea are shown in Table 4. Moisture and ash content mean values are comparable with some reported works in the literature[26,27]. Iron (20.0±0.1 mg/100 g) and mercury (0.2±0.1 mg/100 g) were found to be the high and lowest concentrations in Nasarawa-Ugede and Keffi-Nasarawa roads respectively. Cadmium and mercury were not detected in some locations.

Table 5 depicts summary results of all the studied samples. The coefficient of variation percent (CV%) was very high for every metal in guinea corn, bambara groundnut and cowpea since they were very unevenly distributed in the various food matrices. However, CV%

Table 1: Moisture and ash content(%) and heavy metal composition (mg/100 g) of maize sample

Para-meter	Keffi-nasarawa road	Keffi-abuja road	Keffi akwanga road	Akwanga-lafia road	Akwanga-ugede road	Keffi-kafan-chan road	Range	X	SD	CV%
Moisture	12.0±0.4	9.8±0.2	11.0±0.4	10.0±0.1	11.0±0.3	11.5±0.2	9.8-12.	10.9	0.9	7.8
Ash	1.6±0.2	1.4±0.1	1.7±0.3	1.6±0.4	1.7±0.1	1.6±0.0	1.4-1.7	1.6	0.1	6.8
Fe	2.1±0.3	2.1±0.1	2.8±0.3	2.1±0.5	18.0±0.2	1.6±0.1	1.618.0	4.8	6.5	135.7
Zn	2.8±0.1	3.0±0.4	3.1±0.2	2.5±0.2	3.1±0.1	3.6±0.1	2.5-3.1	3.0	0.4	12.0
Cu	0.35±0.2	0.32±0.3	0.33±0.2	0.38±0.1	0.42±0.3	0.38±0.2	0.320.42	0.4	0.1	12.8
Mn	0.27±0.4	0.03±0.1	0.56±0.1	0.07±0.2	0.17±0.5	0.05±0.1	0.03-0.56	0.2	0.2	106.1
Pb	nd	1.35±0.6	0.85±0.2	0.34±0.1	nd	nd	0.35-1.35	0.9	0.5	59.4
Cd	0.16±0.1	0.17±0.2	0.15±0.5	0.21±0.4	0.22±0.6	0.18±0.2	0.15-0.22	0.2	0.03	15.5
Hg	nd	nd	Nd	nd	nd	nd	na	na	na	na

Mean value ± standard deviation of triplicate determinations
X = Overall mean; SD = Standard Deviation, CV% = Coefficient of Variation percent, nd = not detected; na = not available

Table 2: Moisture and ash content (%) and heavy metal composition (mg/100 g) of guinea corn sample

Para-meter	Keffi-nasarawa road	Keffi-abuja road	Keffi akwanga road	Akwanga-lafia road	Akwanga-ugede road	Keffi-kafan-chan road	Range	X	SD	CV%
Moisture	6.1±0.1	53±0.2	6.5±0.2	6.0±0.0	5.8±0.3	6.0±0.1	5.8-6.5	6.0	0.4	6.6
Ash	3.8±0.0	4.1±0.2	4.3±0.2	4.0±0.0	3.9±0.1	4.1±0.3	3.8-4.3	4.0	0.2	4.3
Fe	1.2±0.1	0.75±0.2	4.0±0.1	3.0±0.1	7.0±0.01	2.5±0.1	0.75-7.0	3.1	2.3	73.5
Zn	3.1±0.3	4.1±0.1	6.0±0.4	10.2±0.1	2.0±0.1	3.8±0.1	2.0-10.2	4.9	2.9	60.1
Cu	0.7±0.1	0.9±0.1	nd	0.6±0.1	0.6±0.3	2.0±0.3	0.6-2.0	1.0	0.6	61.9
Mn	1.0±0.2	0.4±0.1	0.31±0.2	1.4±0.3	nd	2.0±0.1	0.31-2.0	1.0	0.7	69.5
Pb	Nd	2.1±0.3	0.35±0.0	0.8±0.2	1.6±0.1	1.0±0.2	1.0-2.1	1.2	0.7	58.7
Cd	0.2±0.1	0.15±0.0	nd	0.8±0.1	nd	0.9±0.1	0.15-0.9	0.5	0.4	76.9
Hg	0.2±0.1	nd	nd	nd	nd	0.30±0.2	0.1-0.3	0.2	0.1	50.0

Mean value ± standard deviation of triplicate determinations
X = Overall mean; SD = Standard Deviation, CV% = Coefficient of Variation percent, nd = not detected

Table 3: Moisture and ash content (%); and heavy metal composition (mg/100 g) of bambara groundnut sample

Para-meter	Keffi-nasarawa road	Keffi-abuja road	Keffi akwanga road	Akwanga-lafia road	Akwanga-ugede road	Keffi-kafan-chan road	Range	X	SD	CV%
Moisture	5.5±0.3	6.6±0.0	7.1±0.1	5.7±0.3	5.6±0.1	5.9±0.4	5.5-7.1	6.1	0.6	10.6
Ash	5.3±0.01	7.0±0.1	6.5±0.3	5.6±0.01	5.7±0.1	6.2±0.1	5.0-7.0	6.1	0.6	10.5
Fe	3.0±0.02	1.0±0.01	11.0±0.1	2.0±0.1	29.0±0.1	12.0±0.04	1.0-29.0	9.7	10.6	109.4
Zn	1.0±0.01	12.0±0.01	4.2±0.01	1.0±0.3	7.0±0.01	6.0±0.12	1.0-12.0	5.2	4.2	79.0
Cu	3.0±0.01	1.0±0.04	4.0±0.01	7.0±0.03	4.0±0.02	4.1±0.1	1.0-7.0	3.9	1.9	50.5
Mn	1.2±0.01	0.7±0.1	1.0±0.01	0.6±0.1	2.2±0.1	0.5±0.1	0.5-2.2	1.0	1.1	102.8
Pb	1.0±0.1	44.0±0.01	36.0±0.01	20.0±0.01	12.0±0.1	2.0±0.01	1.0-44.0	19.2	16.0	83.4
Cd	nd	1.0±0.01	nd	nd	2.0±0.1	1.0±0.01	1.0-2.0	1.3	0.6	43.4
Hg	nd	1.2±0.01	nd	1.0±0.01	nd	nd	1.0-1.2	1.1	0.2	20.3

Mean value ± standard deviation of triplicate determinations
X = Overall mean; SD = Standard Deviation, CV% = Coefficient of Variation percent, nd = not detected

Table 4: Moisture and ash content (%); and heavy metal composition (mg/100 g) of cowpea sample

Para-meter	Keffi-nasarawa road	Keffi-abuja road	Keffi akwanga road	Akwanga-lafia road	Akwanga-ugede road	Keffi-kafan-chan road	Range	X	SD	CV%
Moisture	4.0±0.0	4.6±0.2	4.2±0.4	4.5±0.1	3.8±0.0	3.5±0.	3.5-4.6	4.1	0.4	10.2
Ash	3.1±0.1	4.5±0.1	4.2±0.2	4.2±0.0	4.4±0.1	13.8±0.0	3.1-4.5	4.0	0.5	12.8
Fe	4.0±0.1	2.0±0.5	11.0±0.1	10.0±0.01	20.0±0.1	3.0±0.01	2.0-20.0	8.3	6.8	82.0
Zn	2.0±0.01	1.0±0.1	4.0±0.2	2.0±0.1	1.0±0.01	6.0±0.31	1.0-4.0	2.7	2.0	73.9
Cu	2.0±0.1	0.48±0.01	0.9±0.1	1.5±0.1	3.5±0.1	3.0±0.4	0.48-3.5	1.9	1.2	62.1
Mn	0.6±0.1	4.5±0.3	3.5±0.01	4.0±0.2	1.0±0.1	nd	0.6-4.5	2.6	1.8	66.6
Pb	6.5±0.1	10.0±0.1	5.0±0.2	15.1±0.1	3.2±0.01	nd	3.2-15.1	8.1	4.7	58.4
Cd	6.5±0.1	nd	nd	1.0±0.1	nd	0.80±0.01	0.5-1.0	0.8	0.5	66.9
Hg	0.2±0.1	0.4±0.1	1.2±0.01	nd	nd	nd	0.2-1.2	0.6	0.5	88.2

Mean value ± standard deviation of triplicate determinations
X = Overall mean; SD = Standard Deviation, CV% = Coefficient of Variation percent, nd = not detected

of zinc (12.0), copper (12.8) and cadmium (15.5%) in maize sample indicated that they were evenly distributed. The most varied metal among the samples was iron (135.7%) in maize closely followed also by iron (109.4%) in bambara

Table 5: Summary results of overall mean value, SD and CV% of studied samples from different locations

	Maize			Guinea corn			Bambara goundnut			Cowpea		
Paramete	X	SD	CV%	X	SD	CV%	X	SD	CV%	X	SD	CV%
Moisture	10.9	0.9	7.8	6.0	0.4	6.6	6.1	0.6	10.6	4.1	0.4	10.2
Ash	1.6	0.1	6.8	4.0	0.2	4.3	6.1	0.6	10.5	4.0	0.5	12.8
Fe	4.8	6.5	135.7	3.1	2.3	73.5	9.7	10.6	109.4	8.3	6.8	82.0
Zn	3.0	0.4	12.0	4.9	2.9	60.1	5.2	4.2	79.9	2.7	2.0	73.9
Cu	0.4	0.1	12.8	1.0	0.6	61.9	3.9	1.9	50.5	1.9	1.2	62.1
Mn	0.2	0.2	106.1	1.0	0.7	69.5	1.0	1.1	102.8	2.6	1.8	66.6
Pb	0.9	0.5	59.4	1.2	0.7	58.7	19.2	16.0	83.4	8.1	4.7	58.4
Cd	0.2	0.3	15.5	0.5	0.4	76.9	1.3	0.6	43.4	0.8	0.5	66.9
Hg	na	na	na	0.2	0.1	50.0	1.1	0.2	20.3	0.6	0.5	88.2

X = Overall mean; SD = Standard deviation; CV% = Coefficient of variation percent; na = not available

groundnut. Some heavy metals are not naturally present in food samples but concentrations depend on the soil where they are grown and it has been established that some of them are necessary for life[28-30]. However, when the concentrations of the metals are very high beyond certain tolerable limits, they become toxic. Iron is reported to be very important for normal functioning of the central nervous system[31]. Iron also facilitates the oxidation of carbohydrates, protein and fats. Zinc is present in all tissues of the body and it is a component more than fifty enzymes[32]. The highest overall mean value of iron (9.7 mg/100 g sample) was found in bambara groundnut while the lowest were in guinea corn (3.1 mg/100 g sample). This is an indication that none of the food samples can supply the recommended daily intake of iron[33]. Meanwhile, further work need to be done to find out the reason why iron content in food sample from Nasarawa-Ugede road was exceptionally high (Table 1-4) by studying the iron content in the soils where the crops were grown because it has been reported that iron toxicity effect is more pronounced in acid soils[34]. The overall mean value for zinc were low in comparable with zinc mean value in animal sources[32]. Families and individuals who may be using legume and cereal sources of protein because of low income or in an attempt to cope with inflation may not be able to meet the zinc allowances (about 15-20 mg) per day[35]. Copper and manganese content were very low in all the food samples to cause any deleterious effect in diet with highest mean values of 3.9 mg/100 g and 2.6 mg/100 g in bambara groundnut and cowpea, respectively.

Lead in the form of tetra-ethyl lead, $Pb(C_2H_5)_4$, is the most common additive to petrol to raise its octane member. Upon the combustion of the petrol in the engine, the organic lead is oxidized to lead oxide viz:

$$2Pb\,(C_2H_5)_4 + 27O_2 \rightarrow 2PbO + 16CO_2 + 2OH_2O.$$

The lead oxide, PbO, formed reacts with the halogen carriers (the co-additives) to form particles of lead halides-$PbCl_2$, PbBrCl, $PbBr_2$-which escapes in to the air through the vehicles exhaust pipes. By this, about 80% of lead in petrol escapes through the exhaust pipe as particles while 15-30% of this amount is air borne. Human beings, animals, vegetation and soil are the ultimate recipients of the particulate[36]. The lead level in Nigeria's supergrade petrol is in the range 210-520 mgL^{-1}[20]. The lead content mean value in the studied samples raged from 0.7 mg/100 g in guinea corn to 19.2 mg/100 g in bambara groundnut. Comparison of these lead values (Table 5) with lead values in Agricultural product grown in the middle belt, Nigeria reported by Aremu *et al*[37] showed that lead content in the represent study was too high. When comparing lead content in crops at different locations, high values were recorded in the locations where there were very high volume of traffic. For instance, Keffi-Abuja, Keffi-Akwanga and Akwanga-Lafia roads with very high traffic volume (i.e over 800-1000 velucles per hr) recorded high values of lead content (Tables 1-4). Lead was not even detected in some crops planted along areas of low traffic volume (ie < 200 vehicles per hr) such as Nasarawa-Ugede road. It was noticed that lead concentration was exceptionally high in bambara groundnut at two different areas (Table 3). The reason may be due to soil composition apart from the lead combustion from vehicle exhaust. It was reported that the relative low solubility of lead and its freedom from microbial degradation makes it persistent on the top soils[38]. The greatest lead concentrations are known to occupy in organically rich top horizons of uncultivated soils[39]. The recommended daily intake of lead is 0.430 mg per person[40]. If 20-50 g of farm product collected from those areas where there were very high traffic volume are eaten, the consumer would have consumed 3 to 10 times the recommended daily intake and would have been very harmful.

Patients have been found having elevated amounts of cadmium in their kidneys and arterial walls and an elevated Cd/Zn concentration ratio but whether this is causative is not known. Slight anaemia has been associated with cadmium toxicity. Possibly this occurs because of competition between cadmium and iron in the body resulting in iron deficiency[41,42]. Cadmium overall mean value ranged between 0.2 mg/100 g in maize sample to 0.8 mg/100 g in cowpea (Table 5). It is observed that cadmium was highly concentrated in cowpea sample of Keffi-Kanfanchan road. When comparing these values with agricultural products not planted by the road side[37] there were more concentrations of cadmium in the same food matrices in the current report. Garry *et al*[43] reported that motor vehicles emit cadmium from diesel fuels. Consequently eating 80-100 g food samples planted along the studied areas, would amount to consuming 2 to 3 times the recommended intake of 0.06mg cadmium per person[40]. This suggests that the crops in the present study can contribute significant amount to cadmium toxicity in diet. Fatal effects have been associated with levels of mercury in the kidney of about 0.016 mg g^{-1}[44]. The overall mean value of mercury concentrations were found to be low but still very high when compared with some agricultural products not planted along the roads[37]. However, the recommended intake may be exceeded[40] if about 50 to 60 g of food samples in the current report is eaten per day.

CONCLUSION

In our results food crops planted along the road sides most especially high ways contained Pb, Cd and Hg greater than the above limits, again emphasizing the importance of this type of study. Planting of food crops along the high ways should be discouraged and completely avoided to escape consuming excessive mineral elements from such sources. However, further study need to be done on the mineral analysis of the soils where these food crops were grown.

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