Comparative Assessment of Heavy Metals in Some Selected Foreign and Locally Produced Spices Sold in Apete Market, Ibadan, Nigeria

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Abstract
Spices are being added to foods in Nigeria as ingredients often to improve the color, aroma and acceptability of food. The presence of heavy metals in spices could result in the accumulation of these metals in the body organs. Therefore, this research was carried out to assess the level of trace and heavy metals in frequently consumed spices sold in Apete market, Ibadan, Nigeria. Eight different spices (Garlic, Ginger, Pepper, Seasoning, Onion, Granulated Seasoning, Locust Beans and Karu Funa) were purchased directly at random from the local market in Apete area of Ibadan. After digestion, the determination of trace and heavy metals (Pb, As, Fe, Cu, Zn and Cd) concentration was done using Atomic Absorption Spectrophotometer (AAS). The results showed that Zinc had the highest mean concentration (in mg kg^{-1}) and ranged from 11.62±0.75 (in Seasoning) to 211.07±0.99 (in Locust beans); while Arsenic had the least mean concentration (in mg kg^{-1}) and ranged from 0.02±0.01 (in Garlic and Onion) to 0.85±0.02 (in Seasoning). All metals analyzed except zinc, were found to be within the WHO Maximum Permissible Limit (MPL). Zinc was found to be above the MPL of 50 mg kg^{-1} in Garlic, Pepper, Onion, Granulated seasoning and Locust beans. High level of zinc may pose series of health threat to consumers, as it interferes with the metabolism and activities of other metals in the body. Therefore, routine check and regular monitoring of spices used in food preparation is required to avoid the health risk associated with heavy metals present in spices.

Keywords: Heavy metals, Trace metals, Spices, WHO permissible limits, Apete market.

1. Introduction

Spices are ingredients which do not contain nutritive components but their ability to improve taste and sometimes appearance of food has led to increased usage among locals in Nigeria [1]. They are used for their huge benefits for human health. Many spices have been reported to possess outstanding microbial, antidiabetic, anti-inflammatory, antioxidant and antihypertensive potential [1]. Although spices are important they may contain some toxic chemicals due to accumulation of heavy metals derived from the surroundings of their production, processing and storage conditions [2].

Furthermore, commercial mills may also introduce some quantity of metals into spices as a result of wear and tear of the machine in the course of production [3]. Spices are a potential link of transfering contaminants and heavy metals from the environment to humans through food chain due to their plant origin. These spices may easily be contaminated by heavy metals from the soil or aerial depositions as they are dried on the ground or on roof tops [4]. While low levels of some heavy metals such as Fe, Zn and Cu are considered essential, low levels of other metals such as Cd and Pb can have toxic effects in human biochemical reactions [5]. Heavy metals are important in many respects to man, especially in the manufacturing of certain important products of human use, such as accumulators (Pb), mercury-arch lamps and thermometers (Hg), utensils (Al) and a wide range of other products [6; 7]. But the biotoxic effects, when unduly exposed to them could be potentially life threatening hence, cannot be neglected. While these metals are in many ways indispensable, good precaution and adequate occupational hygiene should be taken in handling them. Although heavy metal poisoning could be clinically diagnosed and medically treated, the best option is to prevent heavy metal pollution and the subsequent human poisoning [8].

Contacts with toxic metals are associated with severe health problems with varying degrees of severity and conditions: Kidney problems, neurobehavioral and developmental disorders, high blood pressure and possibly cancer [1]. [9] noted that since spices and seasoning flavors are frequently and daily used in diets, determining the

level of heavy metals in them is significantly important; because they can have a direct impact on human health.

Besides the common practices of using spices, Nigerians also apply a significant and varied mixture of spices in traditionally prepared powdered foodstuffs such as locust beans, etc. Although Nigeria imports some of the spices found in the Nigerian markets today, there is little information available about the safety of these spices with respect to heavy metals.

Since no study has been conducted to assess the level of heavy metals in food spices of Apete market, this research is therefore, aimed at detecting the levels of heavy metals contamination on the frequently consumed spices sold in Apete market, Ibadan, Nigeria. Moreover, the levels of investigated metals were compared with recommended levels set by international organizations. Monitoring the levels of heavy metals in spices would help ascertain the health impact of consuming these substances, and provide relevant data on spices in the country.

2. Materials and Methods

Sampling and Sample Preparation

Apete is a community which is situated close to the Polytechnic, Ibadan, Oyo State, South west, Nigeria. Apete Market is a public market located in Apete, created majorly for selling food Items to the community. Samples of eight different spices (Garlic, Ginger, Pepper, Seasoning, Onion, Granulated Seasoning, Locust Beans and Karu Funa) were purchased directly at random and identified according to their common and local names from the market in Apete area of Ibadan. The samples of each type were then mixed to form a composite representative sample. Samples were kept in polythene bags and stored in a cool dry cardboard for further experiment.

Digestion and Determination of Metal Concentration

Rinsed several times with tap water to remove any contamination due to detergent; the samples were then soaked overnight in 6 N HNO_3 (Merck) solutions and finally rinsed several times with deionized water. The samples were carefully opened and dried to constant weight. 1g sample was digested with 20mls of an acid mixture of HNO_3/HCl (Anal grade) in ratio 2:1, and the beaker content was placed on a digesting heating mantle at 105^0C. The samples were heated until the evolution of white fumes. The digest was allowed to cool and after cooling, it was made up to 25mils with distilled water. The concentration of heavy metals [Lead (Pb) Arsenic (As), Iron (Fe), Copper (Cu), Zinc (Zn) and Cadmium (Cd)] was read on bulk scientific Atomic Absorption Spectrophotometer (AAS) at various wavelengths [10].

Statistical Analysis

One-way analysis of variance (One-way ANOVA) was used to compare the differences between the means of heavy metal concentration across the different spices and to ascertain if there is significant difference in the variation of metal concentration across the spices. Statistical significance was defined as $p < 0.05$

Results and Discussion

The results of the trace and heavy metal analysis in Garlic, Ginger, Pepper, Seasoning, Onion, Granulated Seasoning, Locust Beans and Karu Funa in and around Apete market, Ibadan are given in Table 1. For comparison, the Maximum Permissible Limit (MPL), as applied to other food and condiments based on WHO/FAO standards are also given in the table. Maximum limits for trace and toxic heavy metals (Pb, Fe, Cu, Zn and Cd) in spices was obtained from [11] and WHO [12]. The mean concentration (mg kg^{-1}) of the metals (Pb, As, Fe, Cu, Zn and Cd) analyzed in the local and foreign spices ranges as follows: Pb (0.52 – 3.02), As (0.02 – 0.85), Fe (22.07 – 163.85), Cu (5.67 – 18.47), Zn (11.62 – 77.23) and Cd (0.03 – 0.18). The heavy metal with the highest concentration (mg kg^{-1}) was Zinc (211.07) in Locust beans and 167.57 in Onion. While the least concentration of heavy metals was in Garlic (0.02 for Arsenic and 0.03 for Cadmium). The levels of iron, copper and zinc in all the samples were relatively high compared with the levels of lead, arsenic and cadmium present in the different spices. Table 1 also showed that the concentrations of lead, iron, copper and cadmium across the different spices were within the maximum permissible limit. The concentration of zinc in Garlic, Pepper, Onion, Granulated seasoning and Locust beans was above the maximum permissible limit while the concentration of zinc in Ginger, Seasoning and

Karu funa was below the maximum permissible limit.

Table 2 shows the Estimated Daily Intake (EDI) of metals from the consumption of spices. All samples were below the Tolerable Daily Intake (TDI) for the different metals when compared with the result in Table 1.

Table 1: Mean ± Standard Deviation of Trace and Heavy Metal Concentrations in Studied Spice Samples in mg kg^{-1}

Spices	Pb	As	Fe	Cu	Zn	Cd
Garlic [a]	2.82±0.02	0.02±0.01	68.23±0.07	5.67±0.02	77.23±0.25	0.03±0.01
Ginger [a]	0.52.001	0.04±0.02	163.85±0.09	7.63±0.12	12.67±0.22	0.16±0.02
Pepper [a]	2.53±0.01	0.05±0.03	49.62±0.05	10.77±0.09	68.44±0.92	0.18±0.03
Seasoning [a]	2.36±0.01	0.85±0.02	122.04±0.08	12.66±0.12	11.62±0.75	0.05±0.02
Onion [a]	2.29±0.01	0.02±0.00	22.07±0.17	6.23±0.08	167.57±0.62	0.12±0.02
Granulated Seasoning [b]	2.24±0.01	0.09±0.01	141.95±0.57	18.47±0.23	68.66±0.56	0.05±0.01
Locust Beans [a]	3.02±0.05	0.15±0.03	158.23±0.32	17.22±0.15	211.07±0.99	0.29±0.03
Karu Funa[b]	2.65±0.05	0.12±0.02	20.97±40.09	4.25±0.22	36.72±0.71	0.17±0.02
MPL	10	NA	300	20	50	0.2

*NA = Not Available; MPL= Maximum Permissible Limit; a = local spices, b = foreign spices

Table 2: Provisional Tolerable Daily Intake of Heavy Metals

Heavy metals	Concentration (mg/kg day^{-1})	Regulatory body
Pb	0.0005	WHO/FAO, 2009
As	NA	-
Fe	0.8	FAO/WHO, 2009
Cu	NA	-
Zn	NA	-
Cd	NA	-

*NA = Not Available

Lead (Pb)

Figure 1 shows the variation of lead concentration across the different spices studied. Lead content (mg kg^{-1}) of the studied spices ranged between 0.52 in Ginger and 3.02 in Locust beans. The content of Pb in all the studied spices (Table 1) was found to be below the MPL (10 mg kg^{-1}).

The relatively high level of Pb observed in Locust beans might have resulted from accumulation of Pb through air pollution and from some agrochemicals comprising pesticides, such as Lead Arsenates, applied during cultivation [9; 13]. Lead is one of the most recognized toxic environmental pollutant. It reacts or complexes with many biomolecules and adversely affects the reproductive, nervous, gastrointestinal, immune, renal, cardiovascular, skeletal and muscular systems as well as developmental processes [13].

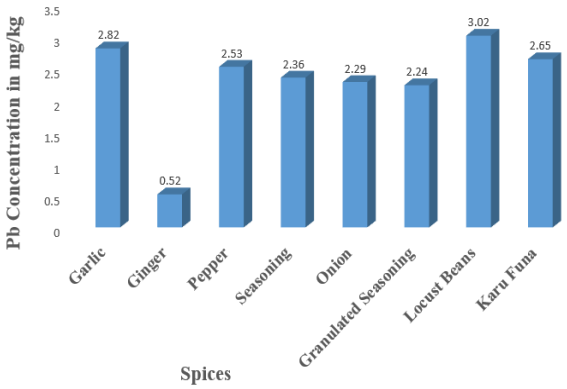

Figure 1: Lead (Pb) concentration across the different Spices studied.

Asenic (As)

Figure 2 shows the disparity in arsenic concentration across the different spices studied. The mean arsenic content (mg kg^{-1}) of the studied spices ranged between 0.02 in Onion (and Garlic) and 0.85 in Seasoning. The concentration of As in all the studied spices generally seems to be very low (Table 1).

Arsenic toxicity symptoms depend on the chemical form ingested [14]. Arsenic acts to coagulate protein, forms complexes with coenzymes and inhibits the production of adenosine triphosphate (ATP) during respiration [15]. It is possibly carcinogenic in compounds of all its oxidation states and high-level exposure can cause death [16; 17]. Arsenic toxicity also presents a disorder, which is similar to, and often confused with Guillain-Barre syndrome, an anti-immune disorder that occurs when the body's immune system mistakenly attacks part of the PNS, resulting in nerve inflammation that causes muscle weakness [18].

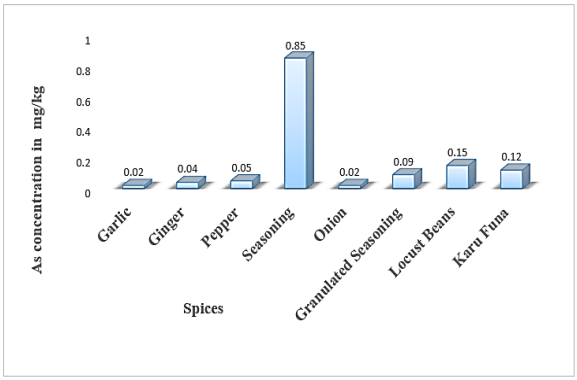

Figure 2: Asenic (As) Concentration across the different Spices studied.

Iron (Fe)

Iron is the most essential element for producing blood cells in the body in a way that 70% of iron is inside blood cells and in the form of hemoglobin with a vital role in transferring oxygen to the human tissues [9]. The level of Fe recorded in the studied spices is relatively very high when compared to the level of the other metals in the spice samples. Iron content of the studied spices (Figure 3) ranged between 20.97 in Karu funa and 163.85 in Ginger. Although the result revealed high levels, the content of Fe in all the studied spices (Table 1) was found to be below the MPL (300 mg kg^{-1}). The comparatively high levels of iron observed in Ginger and Locust beans could be due to contamination during milling. Study shows that grinding of spices in commercial mills contaminates them to about between 3 and 5 folds, due to wear and tear of the machine parts [3]. Iron intake from spices thus has a series of effect on the health of consumers.

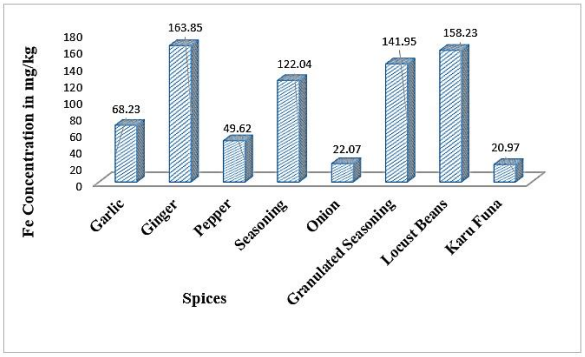

Figure 3: Level of Iron (Fe) in the different Spices studied.

Copper (Cu)

Figure 4 reveals the variation of copper concentration across the different spices studied. Copper content (mg kg^{-1}) of the studied spices ranged between 4.25 in Karu funa and 18.47 in Granulated seasoning. The content of Cu in all the studied spices (Table 1) was found to be below the MPL (20 mg kg^{-1}). Copper plays an important role in growth of bone, connective tissue, brain, heart and many other organs [9]. On one hand Cu plays a role in the oxidative defense system and on the other hand chronic Cu toxicity can result in severe poisoning [2]. The fairly high level of Cu detected in Granulated seasoning and Locust beans demonstrates possible Cu hazard because they are constituents of berbere (a seasoning made up of mixture of spices). On the other hand, pepper can be used as a good source of Cu for consumers because it has relatively high values of Cu.

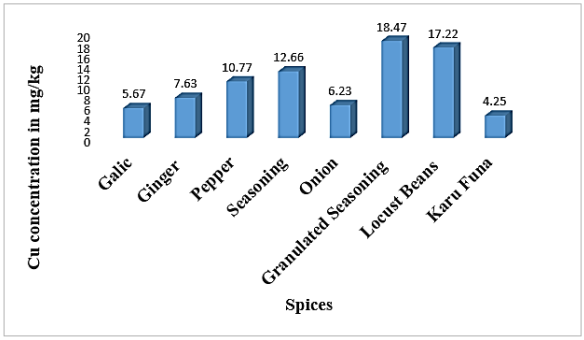

Figure 4: Copper (Cu) concentration across the different Spices studied.

Zinc (Zn)

Zinc is a significant important metal in protein synthesis, energy production, and in maintaining

the membranes [19]. Zn content (mg kg^{-1}) of the investigated spices (Figure 5) ranged from 11.62 in Seasoning to 211.07 in Locust beans. The zinc concentration in the investigated Garlic, Pepper, Onion, Granulated seasoning and Locust beans are above the MPL of 50 mg kg^{-1}while the zinc levels for Ginger, Seasoning and Karu funa are within the tolerable limits (Table 1). The high level of Zn observed in many of the spices may pose a series of health threat to consumers. Zinc has a determining role in the performance of over 300 enzymes in the body, participating in their building or regulating their activities [20]. However, high values of zinc in the body interfere with the metabolism and activities of other metals [9].

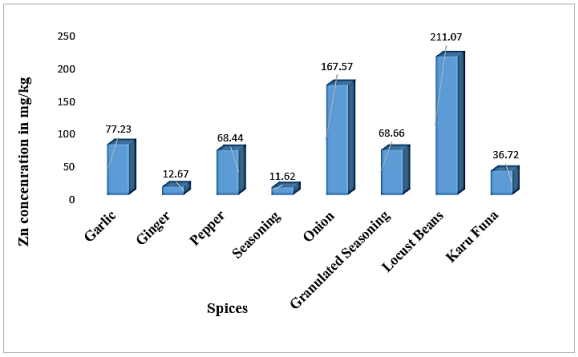

Figure 5: Level of Zinc (Zn) in the different Spices studied.

Cadmium (Cd)

The level of Cd in the studied spices (Figure 6) ranged from 0.03 in Garlic to 0.29 mg Kg^{-1} in Locust beans. As shown in Table 1, Cd content in nearly 90% of the studied spices was found to be within the MPL (0.2 mg kg^{-1}) except the Cd level in Locust beans (0.29 mg kg^{-1}). This high level of Cd in Locust beans might be due to the use of cadmium containing fertilizers or from the practice of growing these crops on the soil amended with sewage sludge [2]. The high levels of Cd may also be associated with the plant and the soil properties (such as calcareous nature of soil) that affect uptake of the metal [5]. High value of Cd in the body induces kidney injuries, leading to aminoaciduria, glycosuria and renal tubule necrosis [21].

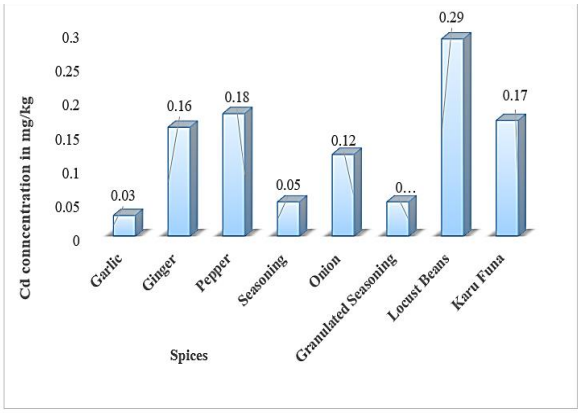

Figure 4: Cadmium (Cd) concentration across the different Spices studied.

Conclusion

Spices include the leaves, seeds, flowers, and/or other plant parts of herbs containing oils and other chemicals, which give foods characteristic taste and flavours. The zinc levels in Locust beans, Onion and Garlic reported in this research, are much higher than the maximum permissible limit set by World Health Organization/ Food and Agricultural Organizations, and this may contribute to the body burden of zinc among the rural population that consume lots of spices. High level of zinc may pose series of health threat to consumers, as it interferes with the metabolism and activities of other metals in the body. Therefore, routine check and regular monitoring of spices used in food preparation is required to avoid the health risk associated with heavy metals present in spices.

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