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Assessment of Heavy Metal Contamination in Edible Fruit Seeds from Dar es Salaam City, Tanzania

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Abstract: *Rivers are the most vital freshwater resources in the world. In Dar es Salaam city, anthropogenic activity stresses the quantity and quality of water resources especially in heavy metal levels. The heavy metals contamination of rivers, sediments and hence consumable food materials remains a global threat to biodiversity and humans. This study was carried out to assess the heavy metals contamination in Mpiji River water, sediments and hence pumpkin which are irrigated by respective river water. Selected heavy metal (Cd, Cu, Fe, Pb and Zn) were analyzed using an inductively-coupled plasma optical emission spectrometer after* $HNO_3/HCl/H_2O$ *(1:2:3) digestion. The mean concentration of cadmium (Cd) at sampling sites ranges from < 0.001 - 0.03 mg/kg (pumpkin), < 0.001 – 0.04 mg/L (river water) and < 0.001 – 0.06 mg/kg (sediment) while quantity of zinc was detected in ranges from 0.02 – 0.07 mg/L, 2.86 – 2.97 mg/kg and 41.07 – 45.63 mg/kg in water, sediment and pumpking seeds respectively. So continued uses of products contaminated with such heavy metals could be significant sources of human exposure and may be linked with harmful effects. Therefore, recommends there must be regular monitoring of heavy metals in sediment, river water and foodstuffs to prevent excessive accrual in food chain.*

Keywords*: heavy metals, contamination, food chain, fruit seeds, consumption habit*

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I. Introduction

Most of tropical fruits such as watermelon, papaya, guava, pineapple, mango and durian are consumed in the fresh form. They are generally well-known for their nutritional values, which include vitamins and carbohydrates. On the other hand, fruits are extensively identified as good source of a healthy diet and adequate use could help to reduce a wide range of diseases like forms of cancer, stroke, heart disease and other chronic diseases (Craig and Beck, 1999; Goldberg, 2003).

Fruits are normally processed into end products such as jams, jellies, juices, pickles, and food flavors. It is commonly known that the fruit processing sector usually generates a large amount of seeds as wastes. In the past, investigations were undertaken to explore their potential uses in food applications due to their high nutritional value. There are a number of literatures dealt with chemical and nutritional characteristics of fruits about like seed varieties, mineral nutrients, edibility and stability of their oils (Soha, *et al.*, 2010; Aravind, *et al.*, 2003; Yanty, 2007). For instance, pumpkin seeds were reported to contain higher levels of potent phytochemicals, such as sterols, with a great promise for immunomodulation, reproductive health, as well as therapeutic effect over a range of disease. Other studies, shows the intake of the whole extract of pumpkin seed is highly correlated with the reduced benign prostate hyperplasia-associated symptoms (Nwokolo and Sim, 1987; Stevenson, *et al.*, 2007; Glew, *et al.*, 2006). The capability of pumpkin seed as a stimulator of sexual desire has also been demonstrated in a number of studies (Gundidza, *et al.*, 2009). Despite the mentioned health benefits, pumpkin seed oil has been shown to exhibit anti-microbial activity, hence, it is well-suited for improving nutritional benefits in food formulations (Nwokolo and Sim, 1987).

There is large amount of waste materials, chemicals or effluents that are introduced into the environment through several sources including discharge into water bodies (Paivoke, 2002). Some of these substances contain toxic heavy metals such as cadmium, lead, copper and arsenic which are known to be toxic with no beneficial effects to man and wildlife (Tyler, 1981). Heavy metals have the ability to accumulate in living organisms and at elevated levels they can be toxic to living organisms. Elevated levels of copper have been reported to cause brain damage (Paivoke, 2002).

The effect of heavy metal contamination of fruit and hence to fruit seeds cannot be underestimated as these foodstuffs are important components of human diet. However, the intake of heavy metal-contaminated fruit seeds may pose a risk to human health; hence the heavy metal contamination of food is one of the most important aspects of food quality assurance (Radwan, and Salama, 2006). Heavy metals, in general, are not biodegradable, have long biological half-lives, and have the potential for accumulation in different body organs, leading to unwanted side effects. Plants take up heavy metals by absorbing them from airborne deposits on the parts of the plants exposed to the air from the polluted environments as well as from contaminated soils through root systems. Also, the heavy metal contamination of fruit and vegetables may occur due to their irrigation with contaminated water.

These heavy metals are a potential human health concern when concentrations are at high levels in soils. Metals may be harmful to humans through ingestion of edible plants containing metals through normal uptake, ingestion of plants splashed with contaminated soil or by accidental direct ingestion of soil usually by children.

Based on their persistence and cumulative behavior as well as the probability of potential toxicity effects, the absorption of heavy metals in human diets as a result of the consumption of fruit seeds means that there is a requirement for the analysis of food items to ensure that the levels of trace heavy metals meet the agreed international standards. This is particularly important for farm products from parts of the world where only limited data on the heavy metal content are available. Knowledge of the contamination of fruit seeds with heavy metals from the Dar es Salaam city has not yet been established; therefore, the present study was undertaken with the aim to compare and investigate the concentration of some specific heavy metals (Pb, Cd, Zn, Cu, and Fe) found in some pumpkin seeds which has gained popularity to most people from this region.

II. Materials and Methods

Collection of the Sample

Three sampling sites (S1, S2, S3) at a distance about 1000 m from each other along the banks of Mpiji River in outskirt of Dar es Salaam city were mapped out for soil, water and pumpkin samples collection. Triplet sample from each site were collected at the interval of one week each 2 – 20th November 2019. Pumpkin and soil samples were collected directly from farms along the bank of the river while water sample was collected in river closer to the garden.

Pummpkin fruits were washed with tap water to remove any dust, sand particles and unicellular algae. Each fruit was crushed to remove the seeds. Then seed was washed several times with tape water until clear water was obtained. Sample was rinsed with de-ionized water and the residual moisture evaporated at room temperature before sun-drying for 2 -3 days on a clean paper with constant turning over to avert fungal growth. Samples were dried in a drying oven, at 105°C, until obtained constant weight then cooled to ambient temperature, crushed by means of a clean pestle and mortar to obtain homogenized samples. The ground samples were then stored at room temperature in airtight sealed polyethylene bags until required for analysis.

Soil samples was collected at depth of about 15cm using hand auger, stored in polyethylene bags and sent to laboratory for oven dried at 60°C for 2 days, followed by grinding with mortar and pestle and sieved using a 2 mm sieve.

Water sampling was done by grab sampling technique, making sure each site sampled in every visit. The sampling time was in the morning and stored in 0.5 L prior cleaned and rinsed with distilled water sampling bottles. Sampling was done in the morning rushed in the laboratories the same day to avoid recreational and other farming activities on the river. Collected samples were immediately transferred to a cool box containing ice packs until the time of filtration, which never exceed 6 hours after collection. All samples were analysed by Inductively Coupled Plasma Optical Emission Spectrometer (ICP - OES) at the Chief Government Chemist Laboratory.

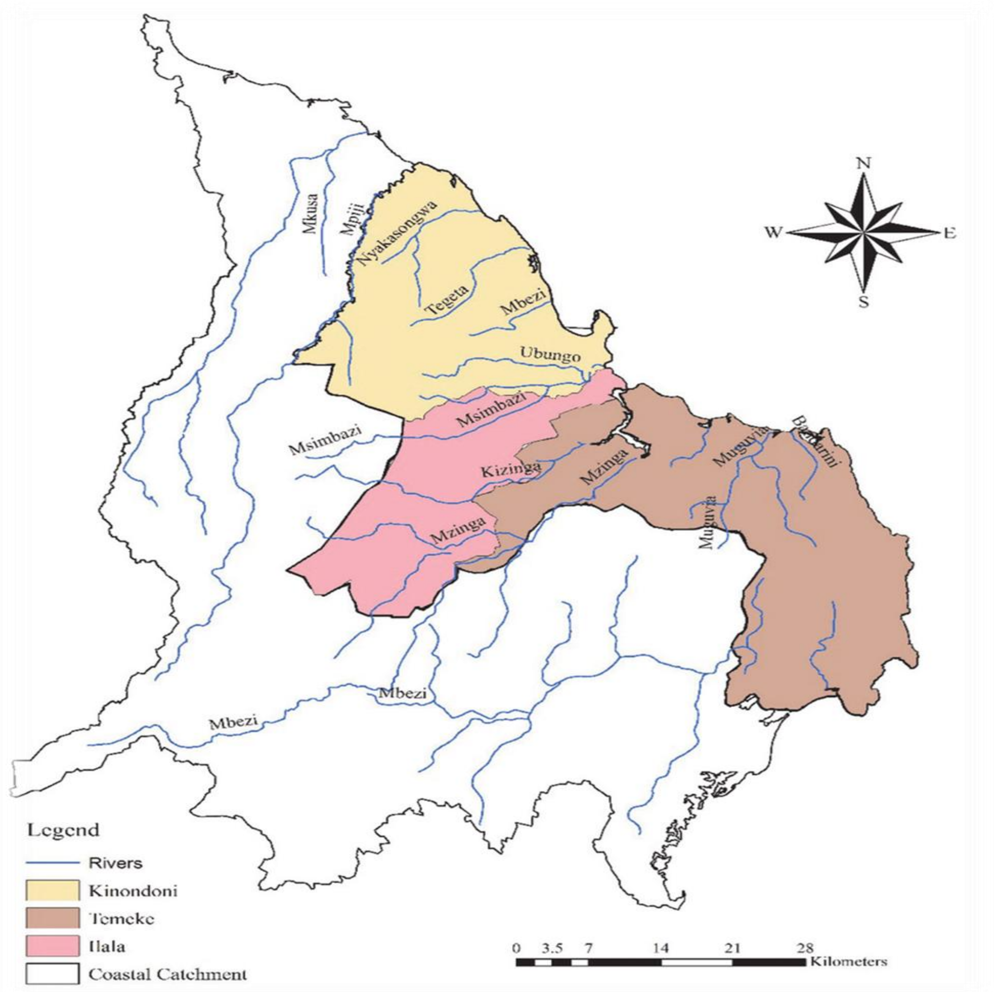

Fig 1: Map of Dar es Salaam City with its surrounding rivers

Seed analysis

About 2.0 g of each of the processed samples was weighed and subjected to dry ashing in a well-cleaned porcelain crucible at 5500 ℃ in a muffle furnace. The resultant ash was dissolved in 5.0 ml of $HNO_3/HCl/H_2O$ (1:2:3) and heated gently on a hot plate until brown fumes disappeared. To the remaining material in each crucible, 5.0 ml of de-ionized water was added and heated until a colorless solution was obtained. The mineral solution in each crucible was transferred into a 100.0 ml volumetric flask by filtration through Whatman No.42 filter paper and the volume was made to the mark with de-ionized water. Then the samples were analyzed by Inductively Coupled Plasma Optical Emission Spectrometer (ICP - OES).

2.1.2 Soil Analysis

About 1.0 g of the oven dried ground sample was weighed into a 250 mL beaker which has been previously washed with nitric acid and distilled water. The sample was reacted with 5mL of HNO_3, 15mL of concentrated H_2SO_4 and 0.3 ml of $HClO_4$ using dropping pipette. The mixture was digested in a fume cupboard, heating continued until a dense white fume appeared which was then digested for 15 minutes, set aside to cool and diluted with distilled water. The mixture was filtered through acid washed Whattman No.44 filter paper into a 50 mL volumetric flask and diluted to mark volume (Yusuf, *et al.* 2015). The sample solution was then aspirated into the Atomic Absorption Spectroscopic machine at intervals.

Quality Assurance

Appropriate safety measures and quality assurance procedures were followed to ensure the reliability of the test results. All the chemicals and reagents used were of analytical and trace-metal grades. Properly cleaned glassware and utensils and distilled water was used during the research. Samples were cautiously handled to minimize the cross-contaminations and reagent blank determinations were carried out to correct the instrument readings.

III. Results and Discussion

The averaged heavy metal concentrations pumpkin seeds are tabulated in Table 1 with the corresponding WHO (2011) and Tanzanian Bureau of Standards (2003). The heavy metal concentrations determined were based on sample dry weight.

Table 1: Average Heavy Metal Concentration in Seed, Water and Soil Samples

Sample	Site	Cd	Cu	Fe	Pb	Zn
pumpkin seed samples (mg/kg d.w.)	S1	< 0.001	0.57	69.70	0.14	44.66
	S 2	0.02	0.72	221.01	<0.01	41.07
	S 3	0.03	0.44	208.19	0.10	45.63
WHO (2011)/TBS (2003)		0.03	2.0/3.00	1.00	0.01/0.05	15.00
Sediment samples (mg/kg d.w.)	S1	< 0.001	0.24	2268.36	< 0.01	2.97
	S2	0.01	0.72	1417.22	< 0.01	2.91
	S3	0.06	0.41	1815.88	0.02	4.86
WHO (2011)/TBS (2003)		0.05	100/3.00	1.00	0.01/0.05	300/150.00
River water samples (mg/L)	S1	0.01	0.76	4.17	<0.01	0.02
	S2	< 0.001	0.58	4.64	0.05	0.04
	S3	0.04	0.74	3.65	0.04	0.07
WHO (2011)/TBS (2003)		0.05	1.50/3.00	0.30	0.10/0.05	15.00/5.00

It was observed that Cadmium (Cd) concentration at S1, S2 and S3 sampling sites ranges from < 0.001 - 0.03 mg/kg d.w. (pumpkin), < 0.001 – 0.04 mg/L (river water) and < 0.001 – 0.06 mg/kg d.w. (sediment). The maximum concentration of Cd was found 0.06 mg/kg d.w in soil at S3 which exceed the WHO and TBS threshold limit. The concentration is extremely far less than those determined earlier (Varsani and Manoj, 2015), found to be found maximum of 2.120 mg/kg d.w in sedment. The level of cadmium level is due to bioavailability and multiple technological applications like batteries, pigments, polymer stabilization, etc. Cadmium when dispersed in the environment can persist in soils and sediments for decades (Bernard, 2008). When taken up by plants, Cd concentrates along the food chain and ultimately accumulates in the body of people eating contaminated food (Bernard, 2008). By far, the most salient toxicological property of Cd is its exceptionally long half-life in the human body. Once absorbed, Cd irreversibly accumulates in the human body, in particularly in kidneys and other vital organs such the lungs or the liver (Johri, *et al.*, 2010).

Lead (Pb) concentration at S1, S2 and S3 sampling station lies in the range of <0.01 - 0.02 mg/kg d.w <0.01 - 0.05 mg/kg d.w <0.01 - 0.14 mg/L in sediment, pumpkin seeds and river water respectively. It was observed the maximum concentration of Pb was 0.14 mg/kg d.w in pumpkin seeds at S1 that is three times higher than the Tanzania acceptable limit. The highest mean concentration is far less than the one detected earlier (Varsani and Manoj, 2015) which was 52.35 mg/kg d.w in soil samples. However, the concentration in river water was inline with the valued detected earlier 0.958mg/l (Dadzie, 2012).

It has been indicated in other study (Brown, and Margolis (2012), the high concentration of Pb is known to impair the proper functioning of the reproductive and nervous systems. Kidney damage, high blood pressure and anemia are consequences of Pb poisoning. Even at very low concentrations, Pb is a threat to public health, because it usually builds up in the body. It is essentially harmful to children under the age of six and causes mental and physical retardation.

Zinc is an essential element for plants and animals, but only a small increase in its level may cause interference with physiological processes. The presence of Zn seems to be essential to neutralize the toxic effects of Cd (Parveen, 2003). In this study, the maximum quantity of zinc was detected in ranges from 0.02 – 0.07 mg/L, 2.86 – 2.97 mg/kg d.w and 41.07 – 45.63 mg/kg d.w in water, sediment and pumpkin seeds respectively. These values correspond to the values obtained earlier in fruits by Basha (2014) where the highest and lowest zinc concentrations were observed in C. limetta (9.2 mg/kg) and S. lycopersicum (3.1 mg/kg) respectively. The maximum level detected in pumpkin seeds, is three times higher than acceptable limit by WHO and TBS (15.00 mg/L).

The mean concentration of copper (Cu) at sampling sites S1, S2 and S3 sampling station lies in the range of 0.24 – 0.72 mg/kg d.w, 0.44- 0.72 mg/kg d.w and 0.58 – 0.76 mg/L in sediment, pumpkin seeds and river water respectively. Comparison of the copper content in all sampling sites is lower than values obtained earlier Elbagermi, et al., (2012), ranges between 0.75 to 6.21mg/kg. Though the concentration was higher than values determined by Mahugija (2018) where copper concentration was 0.039mg/L in water, 0.095 mg/L in mangoe juice and 0.122 mg/L in pipeapple juice. In this study the copper content in the sampling site is not surprising because copper compounds has been used extensively by farmers in agriculture and horticulture as fertilizers and fungicide. Copper contaminated soil is mainly attributed to agriculture activities such as continuous application of copper-based fungicides and pesticides application as fungicidal and bactericidal properties, has been employed as a disinfectant on farms against storage rots and for the control and prevention of certain animal diseases, such as foot rot of animals. Iron (Fe) is an essential metal for most living organisms and humans. It is usually more abundant in freshwater environment than other metals, due to its high occurrence on earth (Forstner and Wittmann, 1979). The deficiency of Fe can lead to anemia and fatigue, which are usually common among children under the age of five, pregnant women and immune compromised individuals, thus making them vulnerable to numerous infections (Garvin, 2015).

The highest range of concentration of Fe was detected in Mpiji river sediment (1417 – 1815.88 mg/kg d.w), while the lowest was detected in river water (3.65 – 4.17 mg/L). The difference observed between river water and sediment can be due to evaporation factor from water body, which can lead to an increase in the concentrations of heavy metal as the dilution factor is removed.

IV. Conclusion

The concentrations of five heavy metals (Fe, Cd, Pb, Zn and Cu) were determined in pumpkin seeds grown at Mpiji River in outskirt of Dar es Salaam city. Samples of pumpkin seeds, Mpiji river sediment and river water used for irrigation were analysed. The high concentrations of the examined heavy metals indicated that these rivers are polluted and highly impacted by surrounding anthropogenic activities like release of partially-treated wastewater effluents houses around Mpiji river, runoffs from agricultural soil, landfill sites very close to the river and other non-point sources. It is recommended that fruit seed should be regularly monitored for the heavy metals. Heavy metals were detected in all samples and based on the results, it is concluded that fruit seeds contain appreciable levels of heavy metals such as Pb and zinc. So continued uses of products contaminated with such heavy metals could be significant sources of human exposure and may be linked with harmful effects. Though levels of Cd was within the WHO acceptable limit, it is hereby not recommended as the body does not have mechanism to eliminate these metals hence increases the risk to consumers.

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