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Determination of Heavy Metals and the Effect of Washing in Tomato (*Lycopersicum Esculentum*) Sold at Two Major Markets in Ado-Ekiti, Nigeria

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Abstract

Tomato (*Lycopersicum esculentum*) is one of the most important vegetable crops grown all over Nigeria. Tomato farming in developing countries is characterized by the indiscriminate application of pesticides and the resultant pollution of agricultural soil with heavy metals that form constituents of these pesticides. These heavy metals have long term toxicity to humans and other biotas in the ecosystem. This problem is exacerbated by a lack of monitoring to regulate the excessive use of chemicals during application. This study was carried out to determine the concentrations of some heavy metals and to compare the effect of washing on tomato samples purchased from two major markets in Ado-Ekiti. The concentrations of some heavy metals (Fe, Zn, Cr, Co, Cd, Mn. Pb, Cu, and Ni) were determined using Atomic Absorption Spectrophotometer (AAS). Results obtained showed the presence of heavy metals (Fe, Zn, Cr, Co, Cd, Mn. Pb, Cu, and Ni) in tomato samples and at different concentrations, with some above the WHO/FAO permissible limits. These results suggest that tomatoes from these locations should be washed thoroughly before it is being considered safe for consumption.

Keywords

Tomato, Heavy Metals, Atomic Absorption Spectrophotometer

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1. Introduction

Fruits and vegetables constitute a significant part of the human diet since they contain carbohydrates, proteins, vitamins, other valuable minerals and trace elements [1, 2]. The consumption of fruits and vegetables are gradually increasing most especially in the urban cities according to Thompson and Kelly [3] while the researched work reported by Duruibe *et al*. [4] and Banerjee *et al*. [5] showed that fruits and vegetables contain both essential as well as non-essential elements, yet among these are some toxic heavy metals (lead, cadmium, mercury, zinc, nickel) that are relatively detrimental to human health. The amount of contaminating deadly heavy metals, as civilization progress nowadays, is now growing at an alarming rate. Murthy *et al*. [6] in his account indicated that toxic heavy metals can interrupt normal physiological functions of the human body by displacing the essential metal ions, blocking the active sites of enzymes and modifying the conformity of proteins in the active body system. Heavy metals are found naturally in the earth and become concentrated as a result of human activities such as industrial production, mining, agriculture and transportation [7, 8]. Although tomato contains both essential and non-essential elements. For instance, heavy

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metals such as copper (Cu), chromium (Cr), cobalt (Co), manganese (Mn) and zinc (Zn) are essential micronutrients for higher animals and plant growth [9]. The presence of heavy metals in the troposphere decreases the growth of bacteria, biomass, and multiplicity. Heavy metals can also cause cardiovascular, nervous, kidney and bone diseases above certain limits [10]. However, at higher concentrations, they can lead to poisoning. On the other hand, lead (Pb), cadmium (Cd) and nickel (Ni) are significant environmental pollutants [11]. These metals cause environmental hazards and are reported to be exceptionally toxic [12]. Studies have revealed that fruits and leafy vegetables are vulnerable to heavy metal contamination from soil, wastewater and air pollution [13]. The trace of lead above 0.05 $mgkg^{-1}$ in fruits and vegetables may cause many signs and symptoms such as abdominal pain, anorexia, hypertension, anxiety, bone pain and brain damage [14]. A lead could also result in children's low Intelligence Quotient (IQ) [15]. The sterilizing, teratogenic and carcinogenic nature of metal could inhibit enzymes with sulfhydryl groups thereby disrupt the paths for oxidative metabolism [16].

Heavy metals such as Cd, Cu, Pb, Cr, Zn, Ni, Co, and Hg cannot be degraded or destroyed and can be accumulated in living tissues through the food chain, causing various diseases and disorders [13]. This fact necessitates for frequent determination of heavy metals in fruits, vegetables to ensure that their levels meet the agreed international standards for the safety of consumers. Fruits, vegetables and other foods are among pathways by which heavy metals enter the human tissues leading to the deterioration of health [17]. The vehicular exhausts, as well as several industrial activities, emit these heavy metals so that soils, plants and even residents along roads with heavy traffic loads are subjected to increasing levels of contamination with heavy metals [8]. Concern has been expressed with regard to the accumulation of toxic heavy metals such as cadmium (Cd), zinc (Zn), copper (Cu), chromium (Cr), mercury (Hg) and lead (Pb) and their potential effects on human health, agriculture and natural eco systems [18]. The tomato that provides a daily and steady supply of vitamins, minerals, and fibre to people in the developing countries are contaminated with high doses of heavy metals, this can pose a serious health risk to millions of people that consume them [19]. Recent studies have shown that heavy metals contamination of food crops and its resultant health consequences is becoming a global issue [20, 21, 22, 23, 24]. There is a paucity of information on the heavy metals contents of vegetable crops from agrochemicals and their health risks in Nigeria. Hence, this study was designed to determine heavy metals (Fe, Zn, Cr, Co, Cd, Mn. Pb, Cu, Ni) contents in tomato purchased from two major markets in Ado-Ekiti, Nigeria for consumption and the effect of washing with distilled water.

2. Materials and Methods

2.1. Study Area

Ado-Ekiti is the capital of Ekiti State. It is an urban town with an increased population due to it being a capital city. The population was 424,340 as of 2012 with an estimated area of 293 square kilometres. The study area is located in two parts of Ado Ekiti in Ekiti State Nigeria. Ago Aduloju with latitude 7°36’9.00”N and a longitude of 5°19’40.44”E, and Shasha along Ikere road with latitude 7°34’18.12”N and a longitude of 5°12’41.76”E.

2.2. Sample Collection

Tomato samples were collected from two different locations (Ago Aduloju and Shasha market) in Ado-Ekiti, Ekiti State in Nigeria. All tomato samples were packed into well-labelled polythene bags and taken to the laboratory for analysis. Tomato samples from each location were divided into three parts (unwashed, washed with distilled water and washed with warm distilled water).

2.3. Sample Preparation and Processing

All glassware and containers required for experimentations were first washed with distilled water. Thus it was ensured that no contamination occurred in them. For the analysis of heavy metals, the method by Chove *et al*. [25] followed with minor modifications was used. Each sample was weighed, dried in an oven at 80°C for several hours. The dried sample was ground in a mortar until it could pass through a 2 mm mesh sieve and stored in clean foil paper. About 2g of the ground sample were placed in a clean porcelain crucible and kept in a cool muffle furnace. The sample was then ashed at 450-500°C for 5hours. The ashed sample was cooled to room temperature in a desiccator. The ash was then dissolved in 5 mL of 20% (v/v) hydrochloric acid. The solution was warmed slowly to dissolve any residues. Filtering of the solution was carried out through an acid-washed Whatman filter paper No 42 into a 50 mL volumetric flask. The filter paper was washed with distilled water and washings collected in the volumetric flask. The resulting solution was diluted to the mark with distilled water, well mixed and used for determination of the heavy metals in tomato samples using Atomic Absorption Spectrophotometer.

3. Results

Table 1. Some guidelines for heavy metals (mg/kg) in tomato samples.

ELEMENT	CODEX (2013)	FAO (2005)
Fe	-	48
Cu	0.30	30
Pb	0.30	5
Ni	67.9	50
Zn	50	60
Cd	0.20	1
Co	-	-
Mn	-	-
Cr	-	5

Table 2. Concentrations (mg/kg) of Heavy Metals in tomato samples.

ELEMENT	AGO-ADULOJU			SHASHA		
	UWS	WSD	WWW	UWS	WSD	WWW
Fe	0.35	0.05	0.03	0.28	0.15	0.07
Cu	0.08	0.04	0.01	0.05	0.03	0.02
Pb	0.20	0.20	BDL	0.01	BDL	BDL
Ni	0.01	BDL	BDL	0.04	0.01	BDL
Zn	0.50	0.10	0.10	0.38	0.31	0.20
Cd	0.03	BDL	BDL	0.02	0.01	0.01
Co	0.01	BDL	BDL	0.01	BDL	BDL
Mn	0.04	0.01	0.01	0.02	0.01	BDL
Cr	0.01	0.01	0.01	0.01	BDL	BDL

*BDL-Below Detectable Limit; UWS-Unwashed sample; WSD-Washed with distilled; WWW-Washed with warm distilled water

4. Discussion

The concentration of Zinc (Zn) in samples from Ago-Aduloju ranged from 0.10 to 0.50 mg/kg and in samples from Shasha ranged from 0.20 to 0.38 mg/kg. The concentration of Zn in the UWS in Ago-Aduloju is present with the highest value (0.50 mg/kg) in both locations which were comparatively found lower than (0.67 mg/kg) as reported by Abdulmojeed and Abdulrahman [26]. The concentration of Zn in the tomato samples (0.38 mg/kg) from the Shasha market was found lower than 0.92 mg/kg as reported by Jimoh and Mohammed [27]. However, the results obtained for Zn in this study did not exceed the limit set by FAO [28] and CODEX [29]. Upon washing with warm distilled water, the level of Zn reduced by 80% and 47% in tomato samples from Ago-Aduloju and Shasha market respectively. Zn is the least toxic among all heavy metals and is an essential element in the human diet as it is required to maintain the proper functioning of the immune system and normal brain activity. Excess of Zinc intake increases the risk of hypertension [30].

Iron (Fe) concentration (mg/kg) in tomato samples from Ago-Aduloju market ranged from 0.35 (UWS); 0.05 (WSD) and 0.03 (WWW) while concentrations of Fe in tomato samples from Shasha market ranged from 0.28 (UWS); 0.15 (WSD) and 0.07 (WWW). Upon washing with warm distilled water, the level of Zn reduced by 91% and 75% in tomato samples from Ago-Aduloju and Shasha market respectively. Fe is beneficial to the human body, it takes part in photosynthesis, respiration, DNA synthesis, and hormone structure and action. It may become an energetic catalyst for some chemical or biochemical processes at a very high concentration.

The concentration of Cobalt (Co) was relatively low in samples from the Ago-Aduloju market as it ranged from BDL to 0.10 mg/kg and in samples from the Shasha market ranged from BDL to 0.10 mg/kg. However, upon washing with warm distilled water, the level of Co reduced by 100% in tomato samples from both Ago-Aduloju and Shasha markets. Moreover, it is well known that Co is beneficial to health, but excess Co may cause lung cancer, nasal cavity and heart effects.

The concentration of chromium (Cr) (0.010 mg/kg) was the same in tomato samples from Ago-Aduloju. Upon washing, the concentration of Cr (0.010 mg/kg) reduced by 100% in tomato samples from the Shasha market. The level of Cr in the sample is the same as the one reported by Ndinwa *et al.* [30]. In this study, Cr showed relatively low concentration in all the samples. Chromium is used in metal plating, stainless steel, wear-resistant, and cutting tool alloys.

Nickel (Ni) concentrations in tomato samples purchased from Ago-Aduloju and Shasha before and after washing are shown in this study. The Ni concentration ranged from BDL to 0.10 mg/kg in tomato samples from the Ago-Aduloju market and BDL to 0.40 mg/kg in tomato samples from the Shasha market. Fortunately, the concentration of Ni in both locations were very low and far less than that recommended (67.90

mg/kg) by the CODEX Alimentarius Commission [29]. Upon washing with warm distilled water, the level of Ni reduced by 100% in tomato samples from Ago-Aduloju and Shasha market.

The concentration of Pb in samples from Ago-Aduloju ranged from 0.20 mg/kg (UWS); 0.20 mg/kg (WSD) and BDL (WWW) while concentrations of Pb in tomato samples from Shasha market ranged from 0.01 mg/kg (UWS); BDL (WSD) and BDL (WWW). The concentration of Pb in an unwashed sample from Ago-Aduloju (0.20 mg/kg) observed in this study showed a lower concentration than the value (2.26 mg/kg) reported by Ndinwa *et al*. [30]. Demirbas [31] reported that the concentrations of Pb in tomato samples collected from the Egyptian market ranged from 0.38 - 0.48 mg/kg which comparatively were found higher than Pb concentration in this study. Upon washing with warm distilled water, the level of Pb reduced by 100% in tomato samples from Ago-Aduloju and Shasha market. Pb may enter the atmosphere during mining, smelting, refining, manufacturing processes and the use of lead-containing products. Lead intake occurs from the consumption of fruit juices, food stored in lead-lined containers, cosmetics, cigarettes and motor vehicle exhaust [30]. Ndinwa, *et al.* [30] found that Pb levels in vegetation increased linearly with traffic density and proximity to roadways. Tomato from these locations are safe for consumption has excess Pb reduces the physical growth and mental growth.

Manganese (Mn) concentrations in tomato samples from Ago-Aduloju and Shasha markets are reported in this study. The concentration, therefore, varied from 0.04 (UWS); 0.01 (WSD); 0.01 (WWW) in samples from the Ago-Aduloju market and 0.02 (UWS); 0.01 (WSD) and BDL (WWW) in samples from Shasha market respectively. Upon washing with warm distilled water, the level of Mn reduced by 75% and 100% in tomato samples from Ago-Aduloju and Shasha market respectively. Moreover, it is well known that a small amount of Mn is needed for growth and prevention of cardiac arrest, heart attack, and stroke, but acute toxicity by Mn causes psychologic and neurologic disorder [27].

The total concentration of Cadmium (Cd) (mg/kg) in tomato samples from Ago-Aduloju market ranged from 0.03 (UWS); BDL (WSD) and BDL (WWW) while concentrations of Cd in tomato samples from Shasha market ranged from 0.02 (UWS); 0.01 (WSD) and 0.01 (WWW). However, it is considered safe for consumption as Cd concentration in both locations were found below the FAO [28] and CODEX [29] regulatory standards. Comparatively, Demirbas, [31] reported that the concentrations of Cd in tomato samples collected from the Egyptian market ranged from 0.61 - 0.71 mg/kg which is found lower than Cd concentration in this study. Upon washing with warm distilled water, the level of Cd reduced by 100% and 50% in tomato samples from Ago-Aduloju and Shasha market respectively. A higher level of Cd may be related to high traffic density. Excess of Cadmium causes health disorders such as lung cancer, kidney damage (necrotic protein precipitation), metabolic anomalies caused by enzyme inhibitions, reproductive failure, damage of central nervous system and DNA [32].

Copper (Cu) concentration in tomato samples ranged from 0.010 - 0.080 mg/kg and 0.020 - 0.050 mg/kg for Ago-Aduloju and Shasha markets respectively. However, all the Cu concentrations were found lower than the FAO [28] and CODEX [29] standards. Demirbas [31] reported that the concentrations of Cu in tomato samples collected from the Egyptian market ranged from 12.9 - 18.7 mg/kg. Upon washing with warm distilled water, the level of Cu reduced by 88% and 60% in tomato samples from Ago-Aduloju and Shasha markets, respectively. Although, Cu has many benefits such as its role as a constituent of metal coenzymes. However, an overdose of Cu may result in acne, anaemia, arthritis, hair loss, adrenal hyperactivity, cancer, diabetes, dyslexia, bone fracture, heart attacks, headaches, hypertension, kidney and liver dysfunction, strokes, vitamin C deficiency and tooth decay [33].

4.1. Variation of Heavy Metal Contents in Tomatoes from Shasha Market

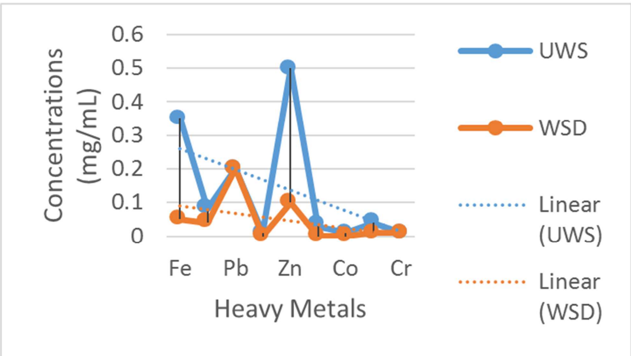

Figure 1. Variation of Heavy Metal content between unwashed sample and washed with distilled water sample

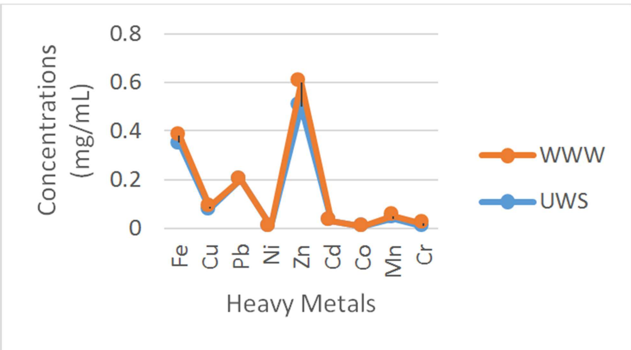

Figure 2. Variation of Heavy Metal content between unwashed sample and washed with warm distilled water sample

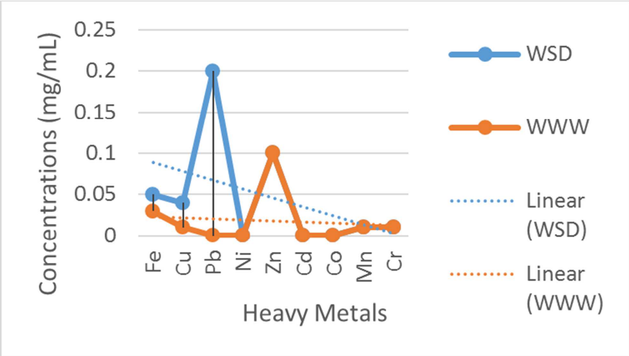

Figure 3. Variation of Heavy Metal content between washed with distilled water sample and washed with warm distilled water sample.

4.2. Variation of Heavy Metal Contents in Tomatoes from Ago-Aduloju Market

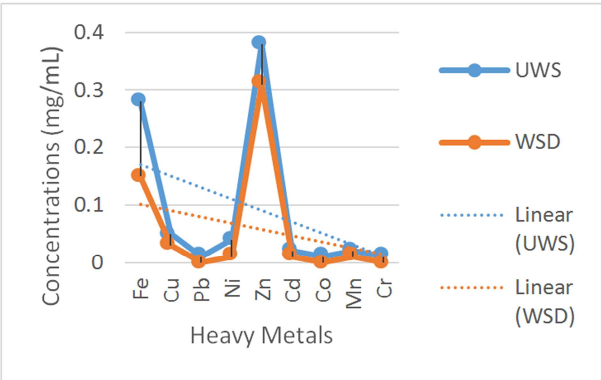

Figure 4. Variation of Heavy Metal content between unwashed sample and washed with distilled water sample

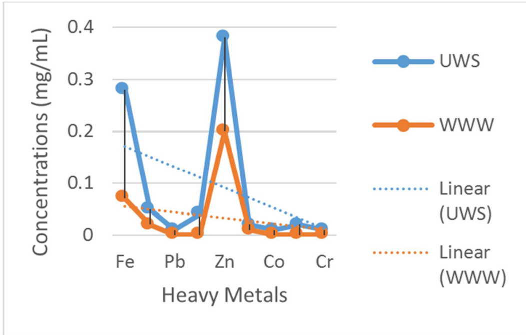

Figure 5. Variation of Heavy Metal content between unwashed sample and washed with warm distilled water sample

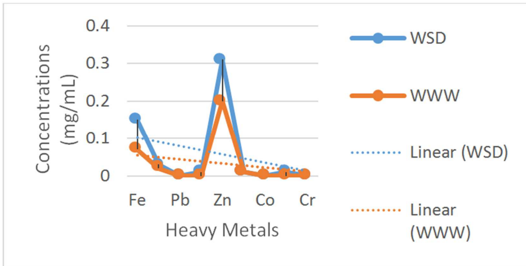

Figure 6. Variation of Heavy Metal content between washed with distilled water sample and washed with warm distilled water sample

4.3. Statistical Analysis

Simple correlation analyses were conducted among various components to show the level of significance from the two locations. There is a strong correlation at significant difference 0.01 > p > 0.05 in all the heavy metals presented in this study.

Table 3. Correlation coefficient between the Heavy Metals concentrations in the tomato samples from Ago-Aduloju market.

Correlations								
	Fe	**Cu**	**Pb**	**Ni**	**Zn**	**Cd**	**Co**	**Mn**
Fe	1							
Cu	-.138	1						
Pb	-.998*	.082	1					
Ni	.998*	-.082	-1.000**	1				
Zn	.998*	-.082	-1.000**	1.000**	1			
Cd	.998*	-.082	-1.000**	1.000**	1.000**	1		
Co	.998*	-.082	-1.000**	1.000**	1.000**	1.000**	1	
Mn	.998*	-.082	-1.000**	1.000**	1.000**	1.000**	1.000**	1

*. Correlation is significant at the 0.05 level (2-tailed).
**. Correlation is significant at the 0.01 level (2-tailed).

Table 4. Correlation coefficient between the Heavy Metals concentrations in the tomato samples from Shasha market.

Correlations									
	Fe	**Cu**	**Pb**	**Ni**	**Zn**	**Cd**	**Co**	**Mn**	**Cr**
Fe	1								
Cu	.999*	1							
Pb	.926	.945	1						
Ni	.990	.996	.971	1					
Zn	.965	.950	.795	.918	1				
Cd	.926	.945	1.000**	.971	.795	1			
Co	.926	.945	1.000**	.971	.795	1.000**	1		
Mn	.613	.655	.866	.721	.386	.866	.866	1	
Cr	-.790	-.756	-.500	-.693	-.923	-.500	-.500	0.000	1

*. Correlation is significant at the 0.05 level (2-tailed).
**. Correlation is significant at the 0.01 level (2-tailed).

5. Conclusion

Heavy metal concentrations were higher in samples collected from Ago-Aduloju than those collected from the Shasha market. The trend between warm water washed (WWW) and unwashed (UWS) tomato samples from Shasha and Ago-Aduloju showed a wide variation, indicating that the tomato samples from Shasha market are better than that of Ago-Aduloju. There was a major decrease in the concentrations of heavy metals on washing off debris from the tomato samples as shown in the result. The levels of heavy metals found in this study were observed to be lower compared to other published works and regulatory standards from different parts of the world. It is evident that tomato samples are at lesser risk from these locations are consider safe for human consumption.

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