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Atomic absorption spectroscopic determination of some heavy metal contents in tomato (*Lycopersicon esculentum* Mill) fruit and water used for irrigation

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ABSTRACT

Concentrations of some heavy metals in mature fruits of tomato (*Lycopersicon esculentum* Mill) grown at Fodugora Farm, Weliso Town (Ethiopia) and Ribu River effluent water, used for its irrigation, have been determined using flame atomic absorption spectroscopic (FAAS) technique. Whereas, the levels of Iron (Fe), Zinc (Zn) and Lead (Pb) in tomato fruits were: 34.05, 4.05 and 1.32 mg/kg respectively, their concentrations in the river effluent water samples were: 95.86, 37.72 and 6.27 mg/L, respectively. The concentrations of Cadmium (Cd) in the studied tomato fruits and irrigating water samples were below the detection limit (0.005 mg/L). Whereas, the Fe and Pb contents of studied tomato fruit as well as water samples were above their respective tolerance limits recommended by FAO and WHO, the levels of Zn and Cd were within their safe limits. A comparison of heavy metal concentrations in the studied systems with the corresponding data reported in the literature is given.

Keywords: Heavy metals, pollutants, irrigation water, tomato fruit.

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INTRODUCTION

Fruits and vegetables constitute an important part of human diet since they contain carbohydrates, proteins, vitamins, minerals and trace elements (Abdulla and Chmielnicka, 1990). In the recent years, due to increased awareness on the food value of fruits and vegetables, their consumption is gradually increasing, particularly among the urban community (Thompson and Kelly, 2003). Although fruits and vegetables contain both essential as well as non-essential elements, yet among these some heavy metals such as: lead, cadmium, mercury, zinc and nickel are cumulative poison posing a worldwide threat (Duruibe et al., 2007; Banerjee et al., 2016). The amount of polluting toxic heavy metals, with progressive industrialization, is now increasing at an alarming rate. The presence of heavy metals in the environment reduces biomass, bacterial growth and diversity. Toxic heavy metals can disrupt normal physiological functions of human body by displacing the essential metal ions, modifying the conformation of proteins and blocking the active sites of enzymes (Murthy et al., 2013). Above certain limits, these metals can also cause cardiovascular, nervous, kidney and bone diseases (Yargholi and Azimi 2008). Lead above 0.05 $mgkg^{-1}$ in fruits and vegetables may cause many signs and symptoms such as abdominal pain, anorexia, anxiety, bone pain, brain damage and hypertension (USDA, 2011). The children exposed to lead may suffer from a diminished Intelligence Quotient (IQ) (Taher, 2003). Cadmium is another toxic metal with sterilizing, teratogenic and carcinogenic effects. It is an inhibitor of the enzymes with sulfhydryl groups that can disrupt the paths for oxidative metabolism (Tortor, 1997) and may lead to cardiovascular disease. Its toxicity affects brain, heart, blood vessels, kidneys and lungs. United State

Department of Agriculture limits 0.01 mg/kg cadmium in fruits and vegetables (USDA, 2011). Heavy metals entering the body through inhalation of dust and consumption of food plants grown at metal contaminated soils, are harmful for the human body and its proper functioning (Jaishankar et al., 2014).

Due to industrial activities, metal contamination of soils may be widely spread in urban areas (Varsani and Manoj, 2015). Wastewater effluents from industries and sewage system in cities and towns are sources of diverse pollutants, including heavy metals. Wastewater irrigation is known to contribute significantly to the heavy metal contamination of cultivated soils and the water bodies, nearby (Singare et al., 2012). These metals, gradually taken up by the plants grown at the wastewater irrigated fields, ultimately, enter the food material (Ismail et al, 2005; Farooq et al., 2008). A prolonged consumption of heavy metals-contaminated food, may lead to accumulation of these metals in the body organs, such as kidney and liver, causing a severe toxicity (Sharma et al., 2006). Domestic waste water discharged from the residential areas and industrial effluents may contaminate the nearby lake or river waters (Singare et al., 2011), therefore, assessment of their pollutant level is necessary in the industrial waste water management (Jadhav and Singare, 2015) and also for the safety of the public health.

Tomato (*Lycopersicon esculentum* Mill) besides being considered an important fruit as well as vegetable has also been reported to have pharmaceutical applications (Debjit Bhowmik et al., 2012). A regular use of tomato in diet decreases the risk of conditions such as cancer, osteoporosis and cardiovascular disease. The area around Weliso town (8°32′ N, 37°58′ E), located in the Debub Mirab Shewa Zone of the Oromia Region (Ethiopia), is famous for the production of large-fruited tomato. The farms around Weliso are irrigated with the water from the Rebu River which passes through the Eastern part of the town. At some points, the untreated Weliso town domestic sewage disposal and industrial effluents from the nearby soap factory enter the Rebu River. Therefore, these may be potential sources of metal pollution in the river water diverted for irrigation purpose of the tomato farms around Weliso. These facts prompted us to determine levels of some heavy metals (Cd, Fe, Pb and Zn) in tomato fruits produces at Fodugora Farm near Weliso town area and also in the river effluent water used for irrigation.

MATERIALS AND METHODS

Equipment

Flame atomic absorption spectrometer (FAAS) (Buck Scientific Model: 210VGP AAS, U.S.A) equipped with deuterium back ground corrector, hollow cathode lamps and acetylene gas as a fuel for the burner; digital analytical balance (Mettler Toledo, Model AG204, Switzerland) and grinder (Moulinex, France).

Chemicals

Nitric acid (HNO_3, MW: 63.01 g/mol, 69 to 72%, Blulux), hydrochloric acid (HCl, Fluka), hydrogen peroxide (H_2O_2, 30%,Scientific Ltd. Northamton, U.K), ferric nitrate [($Fe(NO_3)_3$, BDH], zinc nitrate [($Zn(NO_3)_2$, Fluka], lead nitrate [$Pb(NO_3)_2$, BDH] and cadmium nitrate [($Cd(NO_3)_2$, Fluka] were used as obtained.

Sampling site

The experiments were conducted at Fodugora farming site, 4 km East of Weliso town (8°32′N, 37°58′ E) located at 114 km South-West of the National capital, Addis Ababa, in the Oromia Region of Ethiopia. The collected representative water samples were from different points of the water stream diverted from Rebu River after it crossed Weliso town. Relative positions of Fodugora farming area and samples collection sites are displayed in Figure 1.

Methods

Tomato samples preparation

Mature tomato fruit samples, from ten randomly selected plants, were collected from Fodugora farm during the dry season and the harvesting period January and February, 2014. Each tomato sample, separately, taken in a clean porcelain crucible, was washed thoroughly with distilled water and dried at 85°C for 48 h, in an oven. The dried tomato samples were ground and homogenized into fine powder using a grinding device (Moulinex France) and then stored in polyethylene bags.

Digestion of tomato samples

For optimizing digestion procedure the prepared tomato powder sample (2.0 g) and freshly prepared 2:1 mixture of 70% HNO_3 and 30% H_2O_2 were taken in a 100 ml flask. Various volumes of digesting mixture, temperature and digestion time were tried till clear and colorless digest was obtained. The digest was finally adjusted to 50 ml using deionized water.

Water samples preparation

Each collected water sample (50 ml) was, separately, filtered using a Whatman No.1 filter paper, pre-rinsed with dilute nitric acid. The filtrate was further treated with varying composition of 70% HNO_3 + HCl (5:2 ratio) mixture at 90°C for 6 h till it appeared clear and colorless and then stored it in pre-cleaned polyethylene bottles, at 4°C, before further use.

Sample analysis

Concentration of each metal in the studied samples was determined using flame atomic absorption spectrophotometer (FAAS). Radiation wave length, lamp current, and slit width used in the FAAS were optimized for each metal. After calibrating the instrument, the reagent blanks and samples were aspirated into the atomic absorption spectrophotometer consecutively and a minimum of three readings were taken for each sample and reagent blank solution and the mean value of the concentration signal was used in the subsequent calculations. Metal contents of samples were determined using their respective previously constructed standard calibration curves.

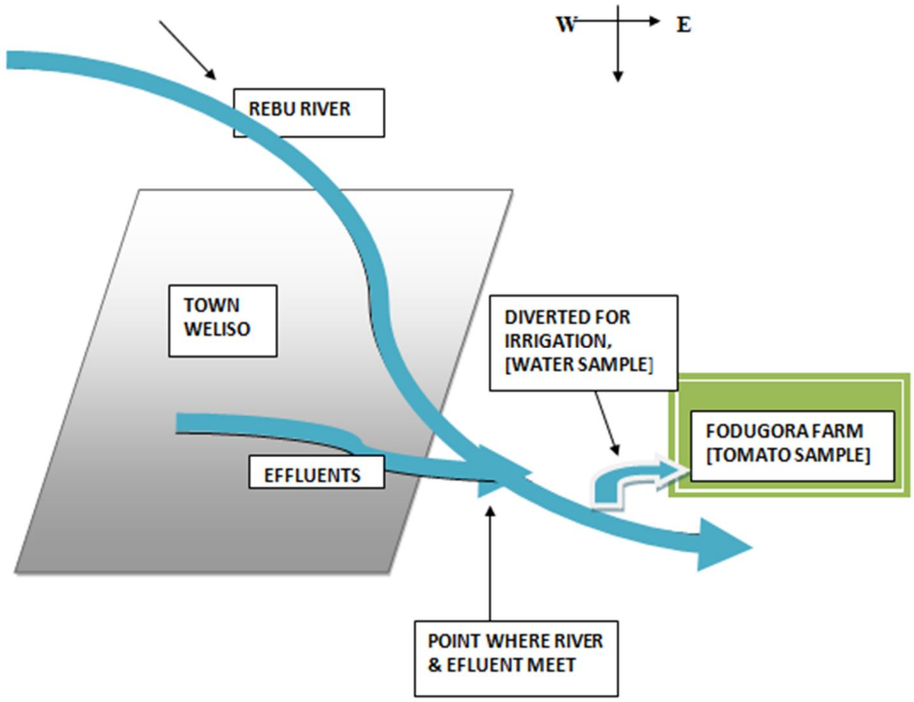

Figure 1. Relative positions of Fodugora farming area and samples (tomato fruits and water) collection sites.

Validation of optimized procedure

Spiking method was adopted for validating the optimized procedure. Spiked samples, in triplicate, were prepared by mixing different volumes of the metal salt solution (10 mg/L) with the powdered tomato sample (2.0 g). The spiked sample was then digested as described for the original samples, made to 50 ml using de-ionized water and analyzed for metal concentration at FAAS. Percent recovery was calculated (Fong et al., 2006) using the relation:

$$R = [(C_s - C) / S].100 \quad (1)$$

Where, C_s = metal concentration of the spiked sample; C = metal concentration of non-spiked sample; S = concentration equivalent of the analyte added to the sample and R = percent recovery

Data analysis

The statistical analysis of the observed data was carried out using the Microsoft Office Excel 2007. Contents of heavy metals in studied samples were determined as the mean of nine replicate measurements. Linear regression and correlation analysis were performed for calculating slope (m) and correlation coefficient (R) of the regression line for each sample.

Precision

The errors in analytical results are generally expressed using precision. The precision of an analytical procedure signifies the extent of closeness of agreement between a set of results. It is usually expressed as the variance, relative standard deviation and percentage relative standard deviation of a series of measurements. In this study, the precision of the results were evaluated by the observed percentage relative standard deviation of the results of three samples (N = 3) and triplicate readings for each sample giving a total of nine measurements for a given bulk sample.

Method detection limit

Method detection limit is the smallest mass of analyte that can be distinguished from statistical fluctuations in the blank, which usually corresponds to the standard deviation of the blank solution times a constant. The detection limit of each metal in the analyzed samples was determined as described, elsewhere (Butcher and Senddon, 1998). After digestion of three blank solutions containing HNO_3, HCl and H_2O_2, three readings were taken for each blank and the mean of these standard deviations was calculated. The method detection limit of each element was obtained using the relation:

$$MDL = 3 \times \delta_{blank} \quad (2)$$

Where, MDL = method detection limit and δ_{blank} = mean standard deviation of the blank readings.

RESULTS AND DISCUSSON

Optimizing tomato digestion procedure

The varying compositions of digesting mixture (70% HNO_3 + 30% H_2O_2), maximum temperature and time

Table 1. The varying compositions of digesting mixture (70% HNO_3 + 30% H_2O_2), maximum temperature and time allowed for optimizing sample digestion condition and the resultant physical appearance of the digest.

Sr. no.	Tomato powder (g)	Composition of digesting mixture			Max. temp. (°C)	Time (min.)	Physical appearance of digest
		HNO_3 (70%), ml	H_2O_2, 30%, ml	Total vol. (ml)			
1	2.0	6.0	3.0	9.0	300	150	Clear and colorless
2	2.0	8.0	4.0	12.0	300	120	Clear but yellowish
3	2.0	7.0	3.5	10.5	300	180	Clear and light yellow
4	2.0	6.0	3.0	9.0	270	150	Clear and colorless
5	2.0	8.0	4.0	12.0	270	120	Clear but yellowish
6	2.0	7.0	3.5	10.5	270	180	Clear and light yellow
7	2.0	**6.0**	**3.0**	**9.0**	**240**	**120**	**Clear and colorless**
8	2.0	8.0	4.0	12.0	240	120	Clear but yellowish
9	2.0	7.0	3.5	10.5	240	180	Clear and light yellow

allowed for optimizing sample digestion condition and the resultant physical appearance of the digest are recorded in Table 1. For digesting 2.0 g dried tomato powder, 9.0 ml digesting mixture, temperature 240°C and digestion time 120 min, were used for the efficient digestion of studied tomato samples.

Sample analysis

Optimization of operating conditions

Optimized operational radiation wave length, lamp current and slit width used in the FAAS measurements, and detection limits for each analyzed metal in studied tomato fruit and water samples are summarized in Table 2.

Calibration of the Instrument

Concentrations of working standard solutions, correlation coefficients (R) and regression equations for the calibration curves for studied metals are summarized in Table 3.

Metal contents

Concentrations of heavy metals measured in studied tomato fruit and water samples are presented in Table 4 and are also compared in Figure 2. Each recorded concentration value was taken as a mean of nine measurements. The maximum permitted values of each metal, by FAO/WHO (2004), in tomato powder and water are also recorded in Table 4. The observed comparative difference of metal level in studied tomato fruit *vis-à-vis* water samples indicates the order of metal uptake by tomato plant as: Fe > Pb > Zn. The observed levels of iron in studied water sample (95.86 mg/L) as well in tomato powder (34.05 mg/kg) were highest among the studied metals. On comparing these with the maximum permissible limit, 0.3 mg/kg, of iron in vegetables by FAO/WHO (2004) guidelines, it may be inferred that tomato samples are heavily contaminated with iron. The observed levels of zinc in the studied water and tomato samples as 37.72 and 4.05 mg/L, respectively, are far below their FAO/WHO's maximum permitted levels, 100 mg/L and 5.0 mg/kg, respectively (FAO/WHO, 2003). The observed lead concentration, 6.27 mg/L, in the effluent water is much higher than 0.01 mg/L, recommended by FAO/WHO (1995). The lead level, 1.32 mg/kg, in the tomato powder samples also exceed the maximum limit, 0.30 mg/kg allowed by FAO/WHO (2004). The cadmium level in studied water as well as tomato powder samples being below the detection limit (0.005 mg/L) indicates that this metal is within the safe limit of the prescribed standards 0.05 mg/kg and 0.003 mg/L for tomato and drinking water respectively, by FAO/WHO (2011).

Validation of optimized digestion procedure

Percent recovery of zinc in spiked water and tomato fruit samples are given in Table 5. The recovery percent of the two types of samples were 96.7 and 93.6%, respectively, within the acceptable range, validate our optimized digestion procedure.

Comparison of results with literature data

Comparison of metal levels in studied tomato samples with the literature data is presented in Table 6. It can be seen that there is a significant variation in the heavy metal contents of tomato fruit reported from different countries. Levels of Fe, Zn and Cd reported from Iran (AEERO, 2008) are higher than those from our work,

Table 2. Optimized operational radiation wave length, lamp current and slit width used in the FAAS measurements, and detection limits for each analyzed metal in studied tomato fruit and water samples.

Element	Wavelength (nm)	Lamp Current (mA)	Slit width (nm)	Detection limit (mg/L)
Fe	248.3	2	0.7	0.030
Zn	213.9	7	0.2	0.005
Pb	283.2	2	0.7	0.100
Cd	228.9	2	0.7	0.005

Table 3. Concentrations of working standard solutions, correlation coefficients and regression equations of the calibration curves for the studied metals.

Metal analyzed	Concentrations of working standards (mg/L)	Correlation coefficient (R)	Regression equation
Fe	1.39, 2.92, 4.12, 8.50	0.9999	Y = 0.00644x – 0.00367
Zn	0.54, 0.98, 1.70, 4.25	0.9998	Y = 0.29017x + 0.003726
Pb	0.22, 0.44, 0.86 ,1.92	0.9984	Y = 0.12028x + 0.1356
Cd	0.23, 0.47, 0.91, 1.76	0.9995	Y = 0.51904x + 0.01243

Table 4. Concentrations of heavy metals measured in studied tomato fruit and water samples, and their maximum permitted values recommended by FAO/WHO (2004) and FAO/WHO (2011), respectively.

Heavy metal	Concentration in dry tomato fruit (mg/kg)	Maximum concentration limt in tomato by FAO/WHO (2004) (mg/kg)	Concentration in studied water (mg/L)	Concentration limit in drinking water by FAO/WHO (2011) (mg/L)
Fe	34.05 ± 0.92	0.30	95.86 ± 2.24	-
Zn	4.05 ± 0.45	5.00	37.72 ± 0.03	100
Pb	1.32 ± 0.02	0.30	6.27 ± 0.003	0.010
Cd	<0.005	0.05	<0.005	0.003

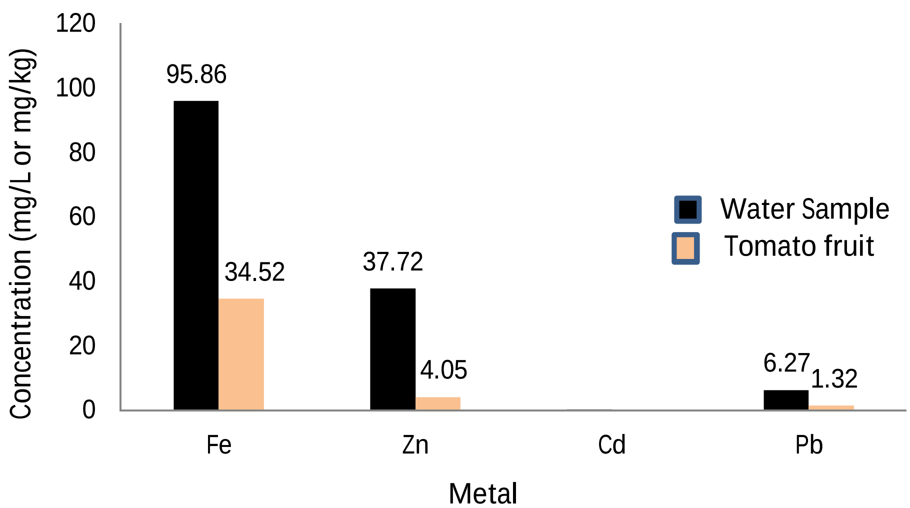

Figure 2. Comparison of Fe, Zn, Cd and Pb concentrations (mg/L) present in studied water and tomato fruit samples.

though, it is reverse in case of Pb. The concentration of zinc found in tomato fruit, in the present study, is higher than those reported from Nigeria. Further, Cd metal in tomato from our study was below its detection limit

Table 5. Percent recovery of zinc in spiked water and tomato fruit samples.

Sample	Concentration of zinc before spiking	Amount added	Amount found	% Recovery
Water	37.72 ± 0.029 mg/L	1.0 mg/L	37.44 ± 0.12 mg/L	96.7
Tomato fruit	4.05 ± 0.45 mg/kg	0.5 mg/kg	4.26 ± 0.0028 mg/kg	93.6

Table 6. Comparison of metal levels in studied tomato fruit samples with the literature data**.**

Country	Concentration, mg/kg				Reference
	Fe	Zn	Cd	Pb	
Nigeria	-	0.67 - 2.54	1.44-1.79	-	AEERO (2008)
Iran	179.80	46.20	1.94	0.01	AEERO (2008)
Present study	34.05	4.05	<0.005	1.32	-

Table 7. Comparison of some heavy metal levels in studied water sample with the literature data.

Country	Metal concentration, mg/L				Reference
	Fe	Zn	Cd	Pb	
Iran	500	200	65	10	AEERO (2008)
Nigeria	6.41 - 28.38	-	0.001 - 0.005	0.54 - 2.10	Galadima et al. (2010)
Nigeria	-	0.62	0.060	0.140	Yahaya et al. (2012)
Nigeria	6.65	0.82	1.420	0.580	Fatoba et al. (2012)[@]
	5.24	0.57	0.190	0.370	Fatoba et al. (2012)[#]
India	-	0.23	0.003	0.015	Singare et al. (2014)[$]
	5.19	5.56	-	0.160	Singare et al. (2013)[&]
This study	95.86	37.72	*ND	6.270	-

*ND = Not detected.
[@]Wastewater from Global soaps and detergents factory, Ilorin.
[#]Wastewater from Dangote cement factory, Ilorin.
[$]Wastewater of Mahul Creek near Mumbai (India).
[&]Water of Bhavan's College Lake of Andheri, Mumbai (India).

(0.005 mg/kg), though, its levels reported from other countries were within 0.14 to 2.0 mg/kg. Finally, the concentration of lead (1.32 mg/kg**)** in tomato fruit, found in the present study, is higher than that reported (0.01 mg/kg) from Iran (AEERO, 2008).

Comparison of some heavy metal levels in studied water sample with the literature data is presented in Table 7. Levels of Fe, Zn, Cd and Pb reported from Iran (AEERO, 2008) are much higher than those from our work. The concentrations of Fe and Zn reported from our study are higher than those reported from Nigeria. Whereas, the level of Cd, in water sample, during the present study, was below its detection limit (0.005 mg/kg), the concentrations reported from Iran (AEERO, 2008) and Nigeria are 10.0 mg/L and 0.1 to 2.1 mg/L, respectively. Singare et al. (2011), in their water pollution study with special reference to the toxic heavy metal content in waste water effluent released from Gove Industrial area of Bhiwandi City located in the Indian state of Maharashtra, have reported that most of the heavy metals including Fe and Cd are much higher than their maximum permissible limits. The levels of Fe, Zn and Pb in water sample in the present study are much higher than those reported by Singare et al. (2013, 2014) in wastewater of Mahul Creek and lake water in Mumbai (India). In this respect, Imam et al. (2017) found that irrigated tomato plants were contaminated by high concentrations of heavy metals zinc, lead, and cadmium over than the stipulated limits given by FAO/WHO (2001). They referred that the consumption of such tomatoes might result to zinc, lead and cadmium toxicity and thereby dangerous to human health.

CONCLUSION

Concentrations of four heavy metals Fe, Zn, Cd and Pb in tomato fruit and the Rebu Riverwater used for irrigation at

Fodugora Farm, Welison Town, Ethiopia, have been determined using flame atomic absorption spectroscopic technique. Whereas, the level of Cd in the two types of analyzed samples are below its detection limit (0.005 mg/L), The lead (Pb) in water and tomato fruit are above the maximum permissible levels reported by FAO/WHO. Therefore, the use of Rebu River effluent water at Fodugora farm for drinking purpose or consumption of tomato grown at the study area may cause health hazard to both humans and animals. Hence, there is a need for sustainable and effective pre-treatment of Weliso town sewage discharge and the industrial effluents entering the Rebu river.

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