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Assessment of horticultural products whose crops allow the use of copper-based pesticides by inductively coupled plasma optical emission spectrometry

Determination of Cu in vegetable by ICP OES

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ABSTRACT

Copper is present in the environment and animals at low levels and is considered an essential microelement for all living organisms, but in high amounts, it is considered toxic. The study's objective was to evaluate the concentration of Cu in different horticultural products marketed in Rio de Janeiro city by inductively coupled plasma optical emission spectrometry. The method provides sensitivity, precision, and accuracy appropriate to assess exposure to Cu due to its intake through ~~fresh~~ vegetable consumption in Rio de Janeiro city. There is no significant statistical difference between Cu concentration in fruits (1.2 ± 0.4 mg kg^{-1}) and non-leaf vegetables (0.9 ± 0.4mg kg^{-1}). The Cu concentration was lower in the root, tuber, and bulb samples (0.7 ± 0.4mg kg^{-1}). All samples allowed by law to use copper-containing pesticides presented concentrations below the limits established by Brazilian regulation. Despite these results, it is crucial to ensure the continuity of the Cu concentrations monitoring in horticultural products in order to prevent harm to human health.

Keywords: copper, spectrometry, horticultural products, pesticides

1. INTRODUCTION

Brazil is the fifth largest country in the world. It has a tropical climate that favors cultivating a wide variety of edible vegetables. It is the third largest producer of fruits in the world, producing about 45 million tons per year. The horticulture activity generates around R$ 25 billion and is responsible for around 7 million direct and indirect jobs (EMBRAPA, 2020). Brazil's ~~fresh~~ produce vegetable market is highly diversified and segmented, with the production concentrated in six species: potato, watermelon, lettuce, onion, and carrots. Family farming accounts for more than half of production. It is estimated that rural properties occupy approximately 448 million hectares (about 53% of the Brazilian territory (Navarro et al., 2020). In these areas, there are policies to increase the produce production to supply national and international markets. However, these policies do not involve environmental and human health concerns, especially due to the extensive use of pesticides (Montagner, 2021)

Studies indicate Brazil has been the world's largest pesticide consumer in absolute numbers since 2008. Between 2000 and 2010, global pesticide consumption increased by 100%, while Brazil's consumption increased by almost 200% (Melo et al., 2020; Bombardi et al., 2017). Additionally, a new regulatory framework for pesticides was launched in 2019, resulting in a record number of pesticides authorizations. In 2020, 493 new pesticides were allowed to be used in crops (MAPA, 2021), thus increasing the risk of food contamination.

Among the authorized substances, inorganic or organic bound to inorganic pesticides can contribute to food contamination, especially by metals. However, these metal-containing pesticides are not the unique reason for metal contamination in edible vegetables. The natural sources and anthropogenic emissions also contribute to food contamination (de Siqueira, 2017). Copper (Cu) is one of the metals present in these formulations and man-made emissions, and it is classified as potentially toxic.

Copper is present in the environment and is essential for all living organisms. It is involved in numerous biological processes. Food is the primary source of Cu exposure by ingestion in humans. However, Cu absorption depends on factors such as the type of food, growing conditions (soil, water, fertilizers, and pesticide use), the amount ingested, chemical form, and the presence of other dietary components, such as zinc (Ellingsenl et al., 2015). Copper in high concentrations is toxic and can cause hepatic dysfunction in the short and long term; convulsions; cognitive dysfunction; cataract, renal disease; cardiac arrhythmia; osteoporosis; gynecomastia; and hyperpigmentation (de Azevedo et al., 2003; ATSDR, 2022). In the environment, Cu in excess can damage plant health, such as root and shoot growth decreasing, reduced number of leaves, altered photosynthesis rates, and changes in chlorophyll and carotenoid levels (Martins, 2014).

One possible way to introduce Cu into the food chain is by using phosphate fertilizers, which pose risks to human health, and fungicides such as Cu hydroxide, copper oxychloride, cuprous oxide, copper sulfate, oxine -copper, and copper carbonate. (ASTDR, 2004; de Siqueira, 2017). The main fungicide approved for production systems in organic farming is a copper-based compound. In 1885, a mixture of copper sulfate ($CuSO_4$) and calcium hydroxide ($Ca (OH)_2$), the Bordeaux mixture, was discovered to control diseases caused by *Plasmopara viticola* in vines. This fungicide continues to be used on a large scale worldwide. (Ghorbani, 2007).

In 2022, the Brazilian Health Regulatory Agency (ANVISA), considering the use of Cu-based compounds and the possible health risks to the population from contaminated food by these compounds, published a rule (RDC nº 722/2022) that establishes the Maximum Residue Limits (MRL) of contaminants in foods, and the analytical methods for conformity assessment. This rule defines the MRL limits for arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg), tin (Sn), copper (Cu), and chromium (Cr). MRL for copper varies from 0.05 mg kg^{-1} in anhydrous milk fats to 40 mg kg^{-1} in cocoa beans. For crops allowed to use copper-based pesticides, the MRL is 10 mg kg^{-1}.

Considering the use of various Cu-based substances in edible crops, this study aimed to evaluate Cu concentration in different ~~fresh~~ produce vegetables marketed at the Central Supply Center of Rio de Janeiro (CEASA-RJ) and assess the Cu exposure due to intake of horticultural products in Rio de Janero City.

2. MATERIAL AND METHODS

The analyzes were carried out in the Inorganic Elements Sector of the Chemistry Department of the National Institute for Quality Control in Health (INCQS) at the Oswaldo Cruz Foundation (FIOCRUZ).

2.1 Food Sampling

The samples of edible vegetables were acquired, from July 2012 to July 2015, from the CEASA-RJ, is the only public commercial distributor in the states of Rio de Janeiro, being responsible for the commercialization of horticultural products for the metropolitan region of Rio de Janeiro. The horticultural products were chosen based in the most selled edible vegetables in Rio de Janeiro State in this period. ~~I~~ 370 samples of different products covering the categories of fruits, non-leaf vegetables and tubers/roots/bulbs were acquired in 10 collections (November 2012; March, June, September, and December 2013; March, June, September, and December 2014; March 2015). The collections were design to cover the respective harvest seasons and the largest possible number of vegetables per collection. At least one kilo of each vegetable category was acquired during collections. Tomato was an exception, where larger amounts where acquired, because two different modes of cultivation where compared, the traditional farming one and the sustainable farming (that promotes soil and water conservation, reduced pesticide application, higher crop yield, and more favorable production mode for the farmer and the environment). The samples fresh were washed with deionized water, homogenized and processed in a blender then portioned into Falcon tubes and stored under refrigeration (2-8ºC).

The parts of the vegetables used to determine the Cu concentration was conducted in according of Codex Alimentarius (CODEX, 2010). **Table 1** shows the quantities of each selected product and the part of the vegetable used for Cu analysis.

~~The samples were homogenized, ground in an industrial-type crusher and stored in appropriate containers~~. To Cu determination, 0.5 g of each sample fresh was weighed in duplicate. The treatment of the samples was conducted according to the AOAC procedure, 2012, Chapter 9, method No. 999.11, which consists in the pre-digestion of the sample with 5 mL of 65% (w/v) nitric acid p.a (Merck, Germany) and 1 mL of 30% (v/v) hydrogen peroxide p.a (Merck, Germany), followed by calcination in a muffle furnace at 450 °C for 12 h, solubilization of the ash with a solution of supra pure nitric acid 10% (v/v) and quantitative transfer with deionized water (Millipore, Brazil) for 15 mL Falcon-type flasks (fine volume 15mL). To assess the quality of the analytical results, the reference material was processed and analyzed in the same way and concomitantly with the samples.

Table 1

2.2. Reagents and reference standards

Standards solution of 1000 mg L^{-1} ± 2 mg L^{-1} the copper brand Sigma-Aldrich were used to intermediate prepare 1000 µg L^{-1}. From these intermediate solutions, a calibration curve was prepared by means of successive dilutions, with a working range of 30 to 400 µg L^{-1}. To guarantee the quality of the results, the National Institute of Standards and Technology (NIST) Spinach leaves - 1570a and Tomato Leaves-1573a reference material were used during all the experiments.

2.3. Equipment

The Cu concentration was determined by inductively coupled plasma optical emission spectrometry – ICP OES (Optima 8300Perkin Elmer, USA) equipped with a GemCones™ nebulizer, cyclonic glass nebulizer chamber. White Martins (São Paulo, Brazil) supplied argon gas with a minimum purity of 99.996%. **Table 2** describes the operational parameters for the Cu determination.

Table 2

2. 4 Statistical analyses

Descriptive statistics were obtained using Microsoft Excel 2010, including the arithmetic mean, median, standard deviation (SD), Student's t-test and analysis of variance (ANOVA). The measurement uncertainties were estimated by the 'bottom-up' mode, in which the identification and quantification of the relevant sources of uncertainty are presented in the cause and effect diagram (Figure 1) (la Cruz et al., 2010; EURACHEM, 2012). Once the final combined uncertainties have been calculated and the coverage factor k (k = 2) was defined at 95% confidence level, the final expanded uncertainty was estimated (Oliveira et al., 2009; la Cruz et al., 2010).

Figure 1

2. 5 Validation

The parameters have been validated according to alidation of Analytical Methods from The Brazilian Institute of Metrology, Standardization and Industrial Quality (INMETRO, 2016) and ISO 17025. The linear range varied from 30 µg L^{-1} to 400 µg L^{-1} and the working range varied from 30 µg L^{-1} to 150 µg L^{-1}. The limit of detection (LOD) and the limit of quantification (LOQ) were obtained by reading 10 solutions independent of the blank and calculated according to the INMETRO guidance document for a 95% confidence level (INMETRO, 2020).

The method accuracy and precision have been determind using reference material Nist 1573a e Nist 1570, according to recommendations from INMETRO. The acceptance criteria vary from 80%–120% of the certified value and the maximum percentage to relative standard deviation (% RSD) was 20% (INMETRO, 2020; ISO, 2017).

2.6 Cu exposure assessment

A deterministic model was used to assess the exposure to the probable daily intake of Cu in fruits and vegetables. This model uses concentration and consumption values, such as the mean, median, 97.5th percentile or maximum value (Jardim, 2009). The Cu concentrations used to calculate the intake were defined as the 97.5th percentile of fruits samples and non-leafy vegetables samples combined, independent of the region. The objective of using the 97.5th percentile was to evaluate the maximum Cu an individual would ingest Cu in one day by consuming contaminated food (Kroes et al., 2002; WHO, 2020)

The data about the consumption of Horticultural products was obtained from the national food consumption data survey conducted by the Brazilian Institute of Geography and Statistics (IBGE). These surveys evaluate the profile of food consumption by families. These data generally do not provide information about the distribution of consumption among individuals and do not consider consumption outside the home or the amount of food wasted (IBGE, 2018). Cu intake is expressed in milligrams of metal per kilogram body weight and was estimated for individuals aged 45–54 years with an average weight of 70 kg, regardless of the region where they live (IBGE, 2020).

In the risk assessment of exposure levels due to the consumption of horticultural products in the southeast Brazilian region, the MOE was calculated by the ratio between the Benchmark Dose Lower Confidence Limit (BMDL) and the Cu intake (Equations 1 and 2). In this evaluation, BMDL (reference dose in which, for the first time, the adverse effect can be observed at the lower limit for a 95% confidence interval) was 0.05 mg kg day^{-1}, as suggested by ATSDR (2022), was considered.

$$\text{MOE} = \frac{\text{Benchmark dose lower limit (BMDL)}}{\text{Estimated intake (Cu)}} \quad \text{(Eq.1)}$$

$$\text{Estimated intake (Cu)} = \frac{\text{Daily Food consumption (g day}^{-1}\text{) X Cu (}\mu\text{g g}^{-1}\text{)}}{\text{body weight of 70 kg}} \quad \text{(Eq. 2)}$$

3. RESULTS AND DISCUSSION

For the in-house validation of the analytical methodology, ANOVA was performed to determine the significance of the regression and the linearity deviation to confirm the linearity of the analytical curves (**Figure 2**) The p value was < 0.001, shows the regression of the curve was significant (p > 0.05 would demonstrate that there was no linearity deviation). The determination coefficient (R^2) was > 0.9982, indicating that the analytical curves have linearity according to the INMETRO parameters. The LOD was 10 µg $L^{-1}$and the LOQ was 30 µg L^{-1}, values that are suitable for the type of studied sample. **Table 3** presents the accuracy (recovery) and the precision (percent relative standard deviation - % DPR) data obtained from the comparison among the concentrations obtained experimentally of the certified references materials Nist 1573ª e Nist 1570 and the certified values.

Table 3

The final expanded uncertainty for Cu in agricultural produce was 5.3%, with the greatest uncertainty being the repeatability of the methodology – which contributes with 42.9%, followed by the preparation of the sample (26.4 %), calibration curve (24.5%), and reference standards preparation (6.1%) (**Figure 2**). **Table 4** presents the results for determining Cu.

FIGURE 2

Table 4

Grapes presented the highest Cu concentrations with 2.6 mg kg^{-1} ranging from 0.7- 4.7 mg kg^{-1}. The 90th percentile value was 3.9 mg kg^{-1}, which allows us to state only 10% of the samples had Cu concentrations above 3.9 mg kg^{-1}. The higher average concentration in grapes can be explained by the use of Bordeaux mixture. In addition, characteristics such as a higher surface area of the grape and a thinner skin facilitate the metal permeation, which may explain the higher Cu concentration in this type of sample (Philippsen, 2017)

The Cu concentrations in oranges ranged from 0.8 to 2.6 mg kg^{-1}, the mean value was 1.5 mg kg^{-1} and the calculated median was 1.4 mg kg^{-1}. The 90th percentile value was 2.45 mg kg^{-1}, which allows us to state that only 10% of the samples had Cu concentrations above 2.45 mg kg^{-1}. In the orange crops, Bordeaux mixture is also used in order to favor the development of more visually attractive fruits, reducing the deformation and enhace the adequate leaf growth, protecting the plant against harmful microorganisms (EMBRAPA, 2016).

Guava and banana had the second and fourth highest average of Cu, respectively. One of the possible reasons for these Cu levels is the recommendation of preventive spraying in these two crops with cupric fungicides, such as copper sulfate, copper oxychloride, or cuprous oxide, on the fruit. For guava, these are the only pesticides registered for the management of maculate anthracnose (EMBRAPA, 2010). In bananas, these active principles are used to control yellow Sigatoka disease. Furthermore, these fruits easily absorb micronutrients such as iron (Fe), manganese (Mn), zinc (Zn), Cu, and boron (B) (EMBRAPA, 2010)

Pineapple, mango, and apple presented statically different results, with a Cu concentration average below 1 mg kg^{-1}. This value is similar to that described in other studies carried out in different countries, such as Spain (0.8 mg kg^{-1} in fruits), Nigeria (1 mg kg^{-1} in mangoes; 0.8 mg kg^{-1} in pineapple; 0.25 mg kg^{-1} in apples) (Velasco-Reynold, et al., 2008; Filippini, et al., 2018; Onianwa, et al., 2001). In another study carried out in Brazil, the values found in apples were 0.3 mg kg^{-1}, in pineapples were 1.3 mg kg^{-1}, and in mangoes were 1.5 mg kg^{-1} (Ferreira, et al., 2005), similar to results found in this study.

Different concentrations can be explained by several factors such as genetic variety, age, part of the plant and the environment where the agricultural product is planted. Additionally, factors as geoclimatic conditions and anthropogenic activities can also increase Cu concentrations (Santos et al., 2017; Saidelles et al., 2010). Other studies pointed out the food composition can influence the Cu concentration in vegetables. Vegetables with high protein content have higher Cu concentrations (Ferreira et al., 2005). The results found in this study, are in line with this association, because oranges, bananas and guavas, have higher protein levels, and higher Cu concentrations than papaya, which has lower protein levels.

The Cu concentration in strawberries was below 1 mg kg^{-1}, this result indicates the growers are following the guidance for strawberries handling and cultivation, which does not recommend the use of Cu-based pesticides, despite there coumpunds being authorized for foliar application (EMBRAPA, 2016).

The results show no statistical differences, after applying the t-student's test with a confidence level of 95%, between Cu concentrations in traditional tomato farming and in sustainable farming. The Cu concentration found in the sustainable farming samples ranged between 0.3 - 2.8 mg kg^{-1} with an average of 1.0 mg kg^{-1}. When calculating the 90th percentile, the value found was 1.8 mg kg^{-1}. The objective of this production is to increase the shelf life of the fruits, obtain color fruit uniformity, reduce and delay the fruit drop, and present the adequate production system identification of fruits in the market, increasing the product value due to this better appearance. The results are in line with another study (EMBRAPA, 2016), where the Cu concentration ranged from 0.9 to 1.19 mg kg^{-1}, depending on the type of cultivation used.

Non-leaf vegetables and tubers showed no statistical diferrences in Cu concentrations by the ANOVA test. According to Velasco-Reynold et al (2008) the average concentration of non-leaf vegetables and tubers ranged from 0.06 to 2.5 mg kg^{-1}, results wich are equivalent to this study. According to Filippini et al. (2018) Cu concentrations in vegetable samples ranged from 0.24 to 11.44 mg kg^{-1}, Olivares et al. (2004) and Ferreira et al. (2005) this variation was 0.20-2.00 mg kg^{-1} and 0.23-3.25 mg kg^{-1}, respectively. In the work carried out by Onianwa et al (2001), Cu concentrations for non-leaf vegetables ranged from 4.0-12.5 mg kg^{-1} and for tubers from 0.72 to 4.76 mg kg^{-1}, in this case values found are higher than those found in this study.

According to Anvisa, the use of inorganic Cu-based pesticides is allowed in all products analyzed in this study. Despite the immense use of agricultural pesticides in Brazil, all vegetables analised in this paper showed Cu concentrations below the maximum tolerable limit for this food type (10 mg kg^{-1}) defined by ANVISA. This low concentration found in the products may be depending on the type of soil, the amount of organic matter found, the pH, the texture, of the presence of elements such as Fe, Al and Mn and gives kind of and horticultural products. Furthermore, studies show that Cu is fixed to the upper soils part part rich in organic matter, or that it hinders the absorption of Cu by plants (Schramel, 2000; Montavani, 2009).

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3.1 Exposure assessment and risk characterizatio

Table 5 shows estimates of daily Cu intake from horticultural products consumption. Considering the conservative characteristic of this evaluation, values of the 97.5th percentile of Cu concentrations in fruits samples and other samples were used, likewise, according to food consumption data survey.

Table 5

When calculating the MOE to characterise the risk of exposure to Cu, the deterministic approach was used by employing a $BMDL_{10}$ of 0.05 mg kg^{-1} day^{-1}, established by ATSDR in 2022, and a body weight of 70 kg. The MOE exposure margins ranged from 24.27 to 54.34 (**Table 5**).

According to the European Food Safety Authority Scientific Committee (EFSA), only MOE values > 10,000 should be considered of low concern from the point of view of public health and should reasonably be considered a low priority for risk management actions (EFSA, 2005).

4. CONCLUSION

The proposed method has adequate sensitivity, precision, and accuracy to quantify the presence of copper in ~~fresh~~ produce vegetables. The results found shows no statistical differences in the comparison between the Cu concentrations of fruits and non-leaf vegetables, in this study. Root, tuber and bulb samples presented lower Cu concentrations, which can be explained by the agricultural practices applying the Cu-based pesticides on stems, flowers and fruits.

The use of the deterministic model to evaluate exposure had the advantage with regard to the speed and simplicity of the calculations. Nevertheless, this information is important for an initial diagnosis of a risk situation, and there is a need to generate new data. Through this study, we observed that the intake of Cu through agricultural products alone is unlikely to cause health problems.

The results obtained for the analyzed samples showed that the Cu contents in vegetables analised are below the maximum tolerance limit determined by ANVISA indicating a low probability of occurrence of adverse health effects from this source of exposure. Although the low estimated MOE values are not worrisome, however the uncertainties in the characterisation of the risk must be considered and viewed with attention by health agencies. More studies are necessary to determine Cu levels in other types of food to improve the data about populational exposure to this metal.

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FIGURE 1 - Cause and effect diagram (Ishikawa) of the analysis of copper in a sample of fruit and vegetables, indicating the contributions of uncertainty in the quantification of copper.

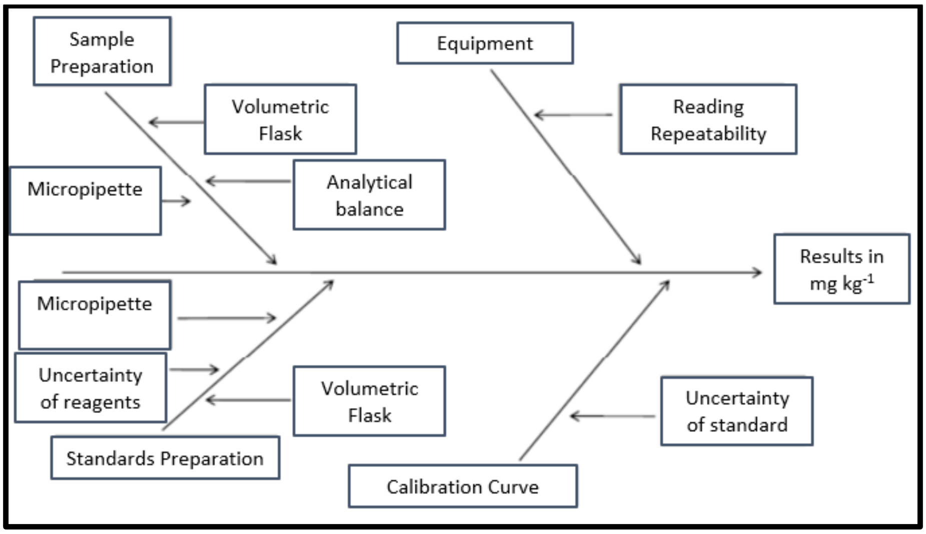


FIGURE 2 - Sources of Uncertainty

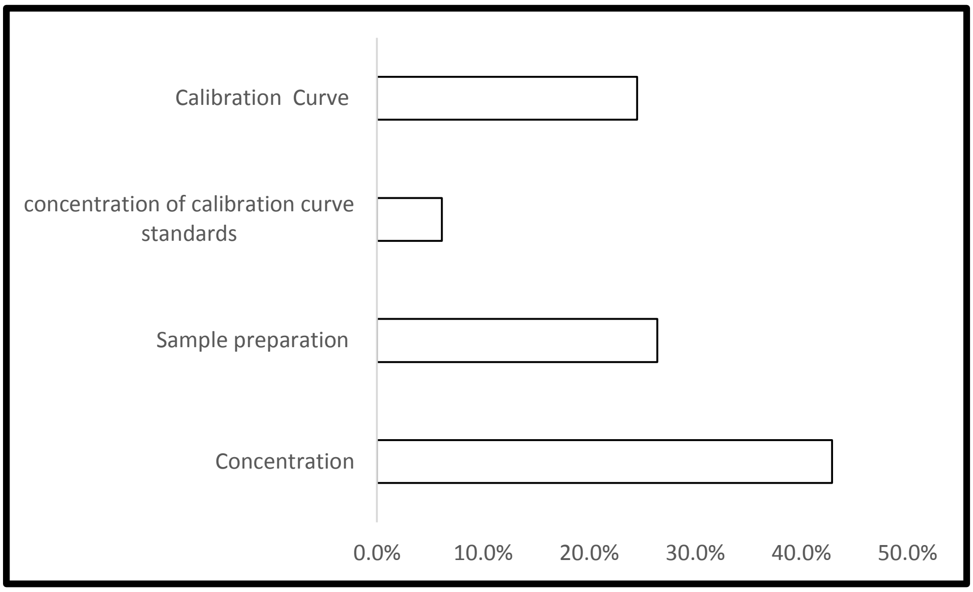


TABLE 1- Horticultural products acquired, number of samples and parts used for Cu determination.

Horticultural products	Nº of samples acquaried	Part used in the analysis
Pineapple	16	Whole product after crown removal
Zucchini	20	Whole product after removing the stalks
Banana	12	Whole product
Potato	12	Whole product
Onion	12	Whole product after removing roots and bark
Carrot	12	Whole product after removing the caps
Guava	15	Whole product
Orange	12	Whole product
Apple	15	Whole product after removing the stalk and seeds
Papaya	12	Whole product
Mango	12	Whole product after removing the pit.
Strawberry	65	Whole product after removal of leaves and stalk
Cucumber	16	Whole product after stalk removal
Pepper	20	Whole product after stalk removal
Tomato	58- sustainable cultivation 23- Traditional Cultivation	Whole product
Grape	30	Whole product after stalk removal

*CODEX,2010

TABLE 2 –Operational parameters for Cu determination by ICP OES.

Operational Parameters	
RF power	1.4 kW
Argon flow rate	
Auxiliary	0.5 $Lmin^{-1}$
Nebulizer	0.2 $Lmin^{-1}$
Plasma	15.0 $Lmin^{-1}$
Reading per replicate	3
Nebulizer	Meinhard
Spray chamber	Cyclonic
Plasma view	Axial
Wavelenght	327.393 nm

TABLE 3. Accuracy and precision Assessment of the analytical method used to Cu determination using the references materials Spinach Leaves (NIST nº 1570a) and Tomato Leaves (Nist nº 1573a), (n = 3).

Reference material	Certified Value	Obtained Value	RSD	Recovery
	mg kg^{-1}		(%)	
NIST nº 1573a	4.7 ± 0.14	4.4 ± 0.5	11	94
NIST nº 1570a	12.22 ± 0.86	12.8 ± 1.0	8	105

Note: % REC, percent recovered; % RSD, per cent relative standard deviation

TABLE 4. Cu Concentration in fresh produce vegetables samples.

Categories	Nº	Agricultural Produce	Cu (mg kg^{-1})			
			Range	Median	Means ± SD	%RSD
Fruits	177	Pineapple	0.2-2.0	0.9	0.9±0.5	55
		Banana	0.7-1.9	1.5	1.3 ± 0.4	31
		Guava	0.7-2.5	1.7	1.7 ± 0.6	35
		Orange	0.8-2.6	1.4	1.5 ± 0.5	33
		Apple	0.2-1.3	0.7	0.7 ± 0.2	28
		Papaya	≤ 0.09-0.76	0.4	0.4 ± 0.2	50
		Mango	0.7-1.3	0.8	0.9 ± 0.2	22
		Strawberry	0.4 – 2.1	0.9	1.0 ± 0.4	40
		Grape	0.7 - 4.7	2.6	2.5 ± 0.9	36
Non-leafy vegetables	157	Tomato	≤ 0.09 - 0.93	0.6	0.6 ± 0.2	33
		Tomato*	0.3 - 2.8	0.9	1.0 ± 0.6	60
		Zucchini	0.6 - 1.3	0.9	1.0 ± 0.3	30
		Cucumber	0.8 - 1.8	0.9	0.8 ± 0.5	62
		Pepper	0.5 - 1.8	1.2	1.1 ± 0.2	18
Root, Tuber and Bulb	36	Potato	0.2 - 1.3	0.6	0.8 ± 0.5	62
		Onion	0.5 - 0.8	0.8	0.7 ± 0.1	14
		Carrot	0.1 - 1.5	0.5	0.6 ± 0.5	83

TABLE 5. Dietary exposure to Cu through fruits and other products.

Region	Type of Agricultural products	Daily Food consumption (g day^{-1})	Cu occurrence µg g^{-1} 97,5th	Estimated intakes Cu (µg kg^{-1} bw day^{-1})	MOE
Southeast	Fruits	57	2.52	2.06	24.27
	Other	60	1.08	0.92	54.34

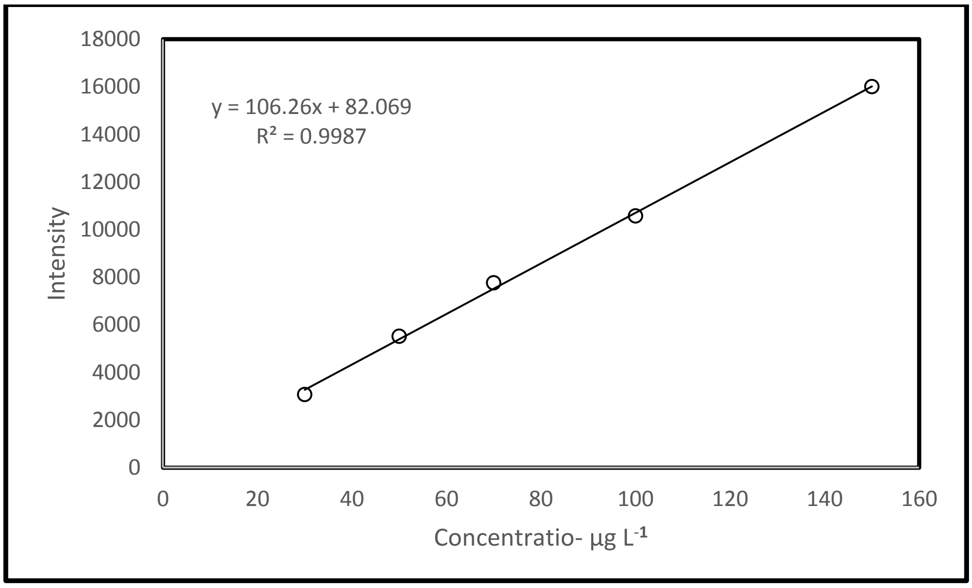
Note: Other = non-leafy vegetables, root, tuber and bulb samples

Supplementary information - Table 1 – Calibration Curve

Linear regression analysis- Y= a + bx.

Angular Coefficient (b):	1.06E+05	**Linear Coefficient (a):**	8.21E+01
r	0.9982	**R^2**	0.9964
N	15	**Degrees of freedom**	13

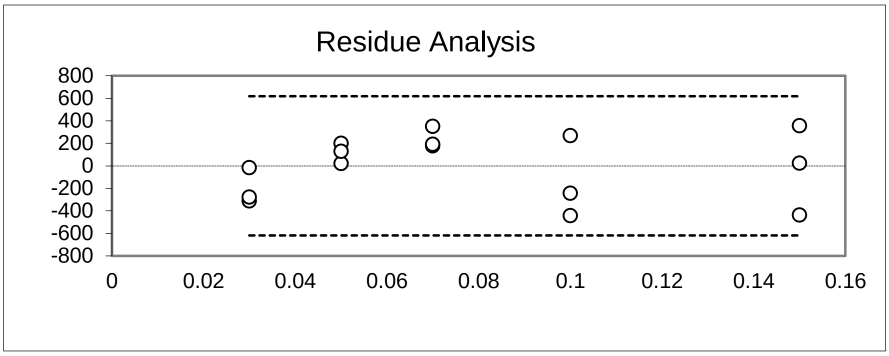
Supplementary information - Figure 1- Calibration Curve



Supplementary information - Table 2- Analysis of variance and Residue Analysis

	G.L.	***SQ***	***MQ***	***F***	***p***
Regression	1	2.98E+08	2.98E+08	3.62E+03	2.71E-17
Residue	13	1.07E+06	8.22E+04		
Ajuste	4	3.95E+05	9.86E+04	1.32E+00	3.35E-01
Error	9	6.75E+05	7.50E+04		
Total	14	2.99E+08			

Supplementary information - Figure 2- Analysis of variance and Residue Analysis



Supplementary information - Table 3- Analytical data from sample analyzes

	Samples	Cu (mg kg^{-1})
Strawberry	1	1.02
	2	1.24
	3	1.33
	4	2.15
	5	1.42
	6	1.28
	7	0.73
	8	0.85
	9	0.89
	10	1.21
	11	0.53
	12	0.92
	13	1.40
	14	0.86
	15	1.15
	16	1.00
	17	0.46
	18	1.47
	19	0.84
	20	0.70
	21	0.54
	22	0.54
	23	0.46
	24	0.63
	25	0.64
	26	0.47
	27	0.71
	28	0.70

29	1.43
30	0.78
31	0.97
32	0.71
33	0.93
34	0.82
35	0.88
36	1.06
37	1.23
38	0.66
39	0.82
40	1.04
41	1.10
42	1.32
43	0.74
44	0.72
45	1.16
46	0.55
47	1.18
48	1.85
49	1.27
50	1.09
51	1.52
52	1.44
53	1.80
54	1.08
55	1.11
56	1.42
57	0.79
58	0.63
59	2.10
60	1.39
61	1.49
62	0.96
63	0.43
64	0.87
65	0.83
Mean	0.99
Median	0.91
SD	0.37
%RSD	38
Minimum	0.43
Maximum	2.10

	Samples	Cu (mg kg^{-1})
Zucchini	1	1.30
	2	1.32
	3	0.85
	4	0.80
	5	1.10
	6	0.72
	7	0.74
	8	0.91
	9	0.78
	10	0.60
	11	0.74
	12	1.30
	13	1.27
	14	0.92
	15	0.73
	16	1.12
	17	1.32
	18	1.23
	19	1.11
	20	0.63
	Mean	0.98
	Median	0.92
	SD	0.26
	%RSD	26
	Minimum	0.60
	Maximum	1.32

	Samples	Cu (mg kg^{-1})
Grape	1	1.85
	2	2.32
	3	2.74
	5	1.06
	6	2.87
	7	0.67
	8	2.15
	9	2.19
	10	2.67
	11	1.55
	12	2.11
	13	2.53
	14	2.73
	15	2.52
	16	2.80
	17	3.97
	18	2.57
	19	2.73
	20	3.35
	21	4.69
	22	3.51
	23	4.40
	24	3.25
	25	3.04
	26	1.67
	27	2.59
	28	0.71
	29	1.22
	30	1.66
	Mean	2.49
	Median	2.57
	SD	0.98
	%RSD	39
	Minimum	0.71
	Maximum	4.69

	Samples	Cu (mg kg^{-1})
Guava	1	0.87
	2	2.13
	3	2.17
	4	1.24
	5	1.88
	6	2.49
	7	1.03
	8	2.52
	9	0.72
	10	1.74
	11	1.13
	12	1.26
	13	2.20
	14	2.24
	15	1.71
	Mean	1.69
	Median	1.74
	SD	0.60
	%RSD	36
	Minimum	0.72
	Maximum	2.52

	Samples	Cu (mg kg^{-1})
Tomato	1	0.850
	2	0.519
	3	0.930
	4	0.319
	5	0.800
	6	0.525
	7	0.933
	8	0.548
	9	0.527
	10	0.721
	11	0.674
	12	0.775
	13	0.814
	14	0.537
	15	0.630
	16	0.520
	17	0.934
	18	0.688
	19	0.595
	20	0.542
	21	0.070
	22	0.418
	23	0.520
	Mean	0.63
	Median	0.60
	SD	0.21
	%RSD	33
	Minimum	0.07
	Maximum	0.93

	Samples	Cu (mg kg^{-1})
Cucumber	1	0.28
	2	0.29
	3	0.38
	4	0.44
	5	0.50
	6	0.52
	7	0.60
	8	0.69
	9	0.70
	10	0.74
	11	0.79
	12	0.84
	13	1.01
	14	1.47
	15	1.58
	16	1.79
	Mean	0.79
	Median	0.69
	SD	0.46
	%RSD	58
	Minimum	0.28
	Maximum	1.79

	Samples	Cu (mg kg^{-1})
Papaya	1	0.39
	2	0.31
	3	0.07
	4	0.16
	5	0.15
	6	0.18
	7	0.39
	8	0.67
	9	0.76
	10	0.46
	11	0.57
	12	0.53
	Mean	0.39
	Median	0.39
	SD	0.22
	%RSD	57
	Minimum	0.07
	Maximum	0.76

	Samples	Cu (mg kg^{-1})
Apple	1	0.23
	2	0.62
	3	0.71
	4	0.68
	5	1.01
	6	0.83
	7	1.28
	8	0.64
	9	0.82
	10	0.51
	11	0.66
	12	0.64
	13	0.56
	14	0.67
	15	0.33
	Mean	0.68
	Median	0.66
	SD	0.25
	%RSD	37
	Minimum	0.23
	Maximum	1.28

	Samples	Cu (mg kg^{-1})
Pineapple	1	0.24
	2	0.45
	3	0.56
	4	0.42
	5	0.65
	6	0.56
	7	0.49
	8	0.88
	9	0.89
	10	1.59
	11	1.49
	12	2.00
	13	1.45
	14	1.03
	15	0.88
	16	1.28
	Mean	0.93
	Median	0.88
	SD	0.50
	%RSD	54
	Minimum	0.24
	Maximum	2.00

	Samples	Cu (mg kg^{-1})
Mango	1	1.01
	2	1.11
	3	1.05
	4	0.67
	5	0.94
	6	0.76
	7	0.80
	8	1.08
	9	0.78
	10	0.87
	11	0.79
	12	1.27
	Mean	0.93
	Median	0.91
	SD	0.18
	%RSD	19
	Minimum	0.67
	Maximum	1.27

	Samples	Cu (mg kg^{-1})
Banana	1	1.36
	2	0.71
	3	1.86
	4	1.45
	5	1.15
	6	0.88
	7	1.13
	8	1.85
	9	0.693
	10	1.56
	11	1.76
	12	1.14
	Mean	1.30
	Median	1.26
	SD	0.41
	%RSD	32
	Minimum	0.69
	Maximum	1.86

	Samples	Cu (mg kg^{-1})
Orange	1	0.84
	2	1.52
	3	1.54
	4	1.54
	5	1.16
	6	1.56
	7	2.59
	8	1.37
	9	0.96
	10	1.64
	11	0.98
	12	2.53
	Mean	1.52
	Median	1.53
	SD	0.56
	%RSD	37
	Minimum	0.84
	Maximum	2.59

	Samples	Cu (mg kg^{-1})
Pepper	1	1.16
	2	0.98
	3	1.42
	4	1.32
	5	1.09
	6	0.52
	7	0.98
	8	1.02
	9	0.99
	10	1.77
	11	0.95
	12	1.23
	13	0.97
	14	1.64
	15	1.06
	16	0.99
	17	1.23
	18	0.98
	19	0.97
	20	1.12
	Mean	1.12
	Median	1.04
	SD	0.27
	%RSD	24
	Minimum	0.52
	Maximum	1.77

	Samples	Cu (mg kg^{-1})
Tomato*	1	0.33
	2	0.38
	3	0.40
	4	0.40
	5	0.42
	6	0.46
	7	0.51
	8	0.52
	9	0.59
	10	0.62
	11	0.66
	12	0.68
	13	0.69
	14	0.69
	15	0.69
	16	0.74
	17	0.74
	18	0.78
	19	0.80
	20	0.80
	21	0.83
	22	0.85
	23	0.86
	24	0.88
	25	0.90
	26	0.91
	27	0.91
	28	0.94
	29	0.95
	30	1.01
	31	1.06
	32	1.15
	33	1.17
	34	1.19
	35	1.20
	36	1.28
	37	1.34
	38	1.34
	39	1.36
	40	1.37
	41	1.40
	42	1.41
	43	1.44
	44	1.47

45	1.49
46	1.50
47	1.53
48	1.71
49	1.77
50	1.78
51	1.81
52	2.15
53	2.16
54	2.26
55	2.26
56	2.55
57	2.76
58	2.83
Mean	1.17
Median	0.98
SD	0.61
%RSD	53
Minimum	0.33
Maximum	2.83

	Samples	Cu (mg kg^{-1})
Potato	1	1.34
	2	1.11
	3	0.61
	4	0.67
	5	0.16
	6	0.18
	7	1.12
	8	0.96
	9	1.12
	10	0.2
	11	0.72
	12	1.14
	Mean	0.78
	Median	0.84
	SD	0.42
	%RSD	54
	Minimum	0.16
	Maximum	1.34

	Samples	Cu (mg kg^{-1})
Onion	1	0.49
	2	0.61
	3	0.82
	4	0.76
	5	0.77
	6	0.63
	7	0.68
	8	0.82
	9	0.74
	10	0.63
	11	0.5
	12	0.81
	Mean	0.69
	Median	0.71
	SD	0.12
	%RSD	17
	Minimum	0.49
	Maximum	0.82

	Samples	Cu (mg kg^{-1})
Carrot	1	1.52
	2	0.71
	3	0.15
	4	0.11
	5	0.35
	6	0.55
	7	0.52
	8	0.62
	9	0.61
	10	0.45
	11	0.59
	12	0.51
	Mean	0.56
	Median	0.54
	SD	0.35
	%RSD	64
	Minimum	0.11
	Maximum	1.52