

Estimation of Some Trace Metals in Commercial Fruit Juices in Egypt

Ayman S. M. Hassan*, Tarek. A. Abd El-Rahman, Alaa S. Marzouk

The Central Agricultural Pesticide Lab, 7, Nadi El-Said St., 12618, Dokki, Giza, Egypt

Abstract Some trace metals in fruit juices collected from the Egyptian markets were determined. The amounts of these metals were estimated by atomic absorption spectrophotometry. Metal (viz.: Cd, Cu, Fe, Pb and Zn) contents in the collected samples (apple, guava, mango, orange and peach juices and nectars) were found at different levels. Most of the collected samples had high limits of Fe than the allowed ones. Natural levels of Cu were found in mango and peach juice and nectar samples, while most other collected fruit juices and nectars had higher limits of Cu. All juice and nectar samples had low limits of Zn. The majority of samples were free from any detectable levels of Cd and Pb except few samples. These results indicated that metal contaminations by toxic metals (Cd and Pb) in a large number of juices and nectars were found below the guidelines for fruit juices given by the (commission regulation (EC) No 1881/2006). Although some essential metals are higher than the allowed limits but they may not represent a dangerous case.

Keywords Fruit Juice, Cadmium, Copper, Iron, Lead, Zinc

1. Introduction

Two thousands years before Christ the ancient medicine stated: "here, eat this root, drink this juice" and hence a wise man responded "don't eat synthetics, drink this juice" [1]. Fruit juices are becoming an important part of the modern diet nowadays [2]. These nutritious beverages and juices can play a significant part in a healthy diet because they offer good taste and a variety of nutrients found naturally in fruits. Juices are available in their natural concentrations or in processed forms. These juices are fat-free, nutrient-dense beverages that are rich in vitamins, minerals and naturally occurring phytonutrients that contribute to good health [3]. A hundred percent healthy juice is that having no processed dextrose sugar such as that with cane sugar, high fructose corn syrup, and other synthesized or commercially processed sugar. The natural sugars have been shown to be effective in the success of 100% juice therapy. The negative studies have all been done on fruit drinks with dextrose sugars. Juice therapy involves the consumption of the juice of raw fruit or vegetables. A person may drink juice preventively to stay healthy, to treat a medical condition like cancer, or to produce a certain outcome, such as strengthening the immune system. In the present of industrialization and development, one concern should be the health of the future generation. Children are the most vulnerable age group of

juice contamination in the food chain. Majority of research confirms that 100% juice does not make children overweight.

Major and minor elements are considered as essential nutrients in food. The routine monitoring of the levels of these elements in fruit juices is a common quality control process [4]. On the other hand, the quality of fruit products is diminished with increasing concentration of toxic compounds, environmental pollutants such as toxic metals, especially Pb and Cd. The main source of human exposure to Pb and Cd is food, which is believed to provide about 80-90% of daily doses of these metals [5], [6]. Lead and cadmium toxicity is well documented and is recognized as a major environmental health risk throughout the world. Lead affects humans and animals of all ages, but the affects of lead are most serious in young children. The International Agency for Research on Cancer has identified Cd as a known human carcinogen. Lead and cadmium poisoning results from the interaction of the metal with biological electron-donor groups, such as the sulfhydryl groups, which interferes with a multitude of enzymatic processes. Clinical manifestations of Pb toxicity include symptoms referable to the central nervous system, the peripheral nervous system, the hematopoietic system, the renal system, and the gastrointestinal systems. Cadmium is a cumulative nephrotoxicant that is absorbed into the body from dietary sources and cigarette smoking.

Malnutrition is of major concern for many tropical developing countries. Iron (Fe) deficiency anemia, for example, affects one third of the world population. On the other hand, excessive iron intake has been associated with an

* Corresponding author:

aymansmhassan@gmail.com (Ayman S. M. Hassan)

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overall increased risk of colorectal cancer. Both zinc and copper, two essential trace minerals, perform important biochemical functions and are necessary for maintaining health throughout life. Zinc constitutes about 33 ppm of adult body weight and is essential as a constituent of many enzymes involved in a number of physiological functions, such as protein synthesis and energy metabolism. Zinc deficiency, resulting from poor diet, alcoholism and malabsorption, causes dwarfism, hypogonadism and dermatitis, while toxicity of Zn, due to excessive intake, may lead to electrolyte imbalance, nausea, anemia and lethargy. The adult human body contains about 1.5 - 2.0 ppm of Cu which is essential as a constituent of some metal enzymes and is required in hemoglobin synthesis and in the catalysis of metabolic oxidation. Symptoms of Cu deficiency in humans include bone demineralization, depressed growth, and gastro-intestinal disturbances, among others, while toxicity due to excessive intake has been reported to cause liver cirrhosis, dermatitis and neurological disorders [7].

The aim of the present study was to evaluate the healthiness of the commercial fruit juices and nectars from the point of view of metal contents.

2. Materials and Methods

2.1. Sampling

Collection of fruit juice samples was performed from commercially available markets. Fruit juices samples of five different types (apple, guava, mango, orange and peach) were bought from different supermarkets. The most frequently consumed brands were selected, from local companies during 2012. A total of 45 fruit juice and 45 nectar samples were studied.

2.2. Chemicals, Stock Solutions

All the chemicals used were Analytical Grade Reagents at least. The element standard solutions used for creating the calibration curves were prepared from 1000 mg/L Merck stock solution of the relevant element.

2.3. Instrumentation

Thermo Elemental model: Solar M Atomic Absorption Spectrophotometer was used for all the measurements. The current, wavelength and slit band width of each element were adjusted automatically by the instrument software.

Determination of trace metals in fruit juices samples were performed according to the method of Official methods of analysis [8]. About 1 gram, to avoid the variations in density, of juice sample -in triplicates- was accurately weighed and transferred into Kjeldahl flask and digested with 10 mL of HNO₃ acid and 1 mL of H₂O₂ then made up the volume to 25 mL by deionized water. Percentage recovery tests were carried out for the five metals by spiking 0.05, 0.05, 1.0, 1.0 and 0.1 µg/mL of Cd, Pb, Fe, Cu and Zn; respectively; to the similarly prepared samples as those unknown samples. The

range of these percentage recoveries were between 96% -103% (Table 1).

Table 1. The Limits of Detection and Quantification and Maximum Permissible Limits of Cd, Cu, Fe, Pb and Zn in the Fruit Juices (µg/g) and Percentage Recoveries

| Metal | Cd | Pb | Fe | Cu | Zn |
|----------------------------|----------------------------------|--------|---|--------|--------|
| LOD* | 0.0028 | 0.0130 | 0.0045 | 0.0043 | 0.0033 |
| LOQ** | 0.0093 | 0.0433 | 0.0150 | 0.0143 | 0.0110 |
| MPL*** | 0.05 | 0.05 | 5 | 5 | 5 |
| Percent Recovery | 97% | 96% | 103% | 98% | 96% |
| *Limit of Detection | **Limit of Quantification | | ***Maximum Permissible Limit [9] | | |

3. Results and Discussion

Some types of metal, such as Cu, Fe and Zn, are the naturally essential elements [10]. Other metals, such as Pb and Cd, have no biochemical or physiological importance, so they are considered as very toxic [11]. Lead and cadmium are naturally occurring elements that are hazardous when present at elevated concentrations.

The levels of Cd, Cu, Fe, Pb and Zn the juice of apple, Guava, mango, orange and peach are determined using atomic absorption spectrometry.

Figures 1-5 show the average concentrations of Cd, Cu, Fe, Pb and Zn in apple, guava, mango, orange and peach juices and nectar samples, respectively.

Figure 6 displays the average concentrations of Cd, Cu, Fe, Pb and Zn in the different fruit juices and nectars and their standard deviations in µg/g.

Statistical analyses using the Systat were applied to calculate the differences between the results. From Figures 1-5 one can see that Cd in all juices and nectars is almost not detectable except that in guava juice no7 which reached 0.03 µg/g and orange juice no7 with 0.01 µg/g. The contents of Cd in all juice samples were lower than the maximum permissible levels (0.05 µg/g), and could be compared with the data reported by other authors [4]. Cadmium is present at low levels in most foods, with commodities such as cereals, fruits, vegetables, meat and fish. These foodstuffs are however minor contributors to overall intake of cadmium, as they are eaten in relatively small amounts, and it is unlikely to exceed the allowed daily intake (ADI) for cadmium. Lead was not dominant in all juice and nectar samples. In apple juice number 5 the concentration of Pb was 1.200 µg/g, which was higher than the maximum permissible levels (0.05 µg/g), while other samples had no detected levels of lead (Table 1). Guava juice samples had a range of Pb leveled between 0.03 and 0.05 µg/g and an average of 0.0408 µg/g and standard deviation of 0.0083 and was round or lower than the the maximum permissible levels (MPL). Four orange juices had Pb between 0.03 and 0.07, average of 0.05 µg/g and standard deviation of 0.0183 with only sample no. 8 higher than the MPL (Table 1). Seven of nine orange nectars

involved Pb with a minimum of 0.02 and a maximum of 0.18 $\mu\text{g/g}$ and the mean was 0.0663 $\mu\text{g/g}$. Lead in orange nectar samples no. 7 and 8 (0.12 and 0.18 $\mu\text{g/g}$, respectively), was higher than MPL. Only four peach nectars had a range of Pb between 0.02 and 0.2 $\mu\text{g/g}$, a mean of 0.0668 $\mu\text{g/g}$, and a standard deviation of 0.0888. Peach nectar no. 5 had higher Pb concentration (0.2 $\mu\text{g/g}$) than the MPL. A total of 3 juice and 3 nectar samples of 90 (6.7% each) violating the Pb MPL. Lead contamination of food arises as a result of environmental emissions, such as mining and the now diminished use of leaded petrol [12]. Levels of lead in fruits and vegetables generally are stringently regulated in the European Union (EU) by Fruit Juice Directive 2001/112/EC & 2009/106/EC [9]. A further source of lead in the diet is from food containers containing lead, e.g. storage in lead-soldered cans, ceramic vessels with lead glazes and leaded crystal glass. Finally, the past use of lead as a material for water pipes in many older houses may result in unacceptably high levels in water supplies. The 1998 Drinking Water Directive, in line with World Health Organization recommendations, sets a revised limit of 10 $\mu\text{g/L}$ for lead in drinking water [2]. However, there is still a significant amount of lead piping in premises worldwide.

Essential metals (Fe, Cu and Zn) are likely existed in all fruits and juices. The range of Fe, Cu and Zn concentrations in apple juices and nectars were 4.42-12.82, 0.3-5.94, 4.21-8.2, 0.15-2.46, 0.44-1.96 and 0.33-0.98 $\mu\text{g/g}$, respectively (Figure 1). For guava juices and nectar the ranges were 2.63 -11.70, 0.7 - 7.36, 5.31 - 12.36, 0.88 - 2.14, 0.165 - 2.47, and 0.3 - 0.84 $\mu\text{g/g}$, respectively (Figure 2). Mango juices and nectars had the following ranges for Fe, Cu and Zn, respectively, 3.17 - 17.86, 1.2 - 6.64, 5.2 - 13.64, 0.91 - 1.24, 0.48 - 2.51, and 0.31 - 0.823 $\mu\text{g/g}$, respectively (Figure 3). Concentration ranges for Fe, Cu, and Zn in orange juices and nectars were 3.3 - 16.48, 0.8 - 4.66, 1.24 - 4.31, 0.16 - 0.93, 0.32 - 1.62, and 0.39 - 0.83 $\mu\text{g/g}$, respectively (Figure 4). The juices and nectars of peach iron, copper and zinc concentrations were between 2.700 - 12.43, 1.33 - 3.620, 1.82 - 5.36, 0.39 - 0.78, 0.6 - 1.22, and 0.44 - 0.99 $\mu\text{g/g}$, respectively (Figure 5). Thirty three juice samples of 45 had higher concentrations of Fe than the MPL (5 $\mu\text{g/g}$), 23 of samples had higher Fe than the MPL. The concentrations of Cu in 25 juice samples were higher than the MPL (5 $\mu\text{g/g}$). All the nectars contained less Cu than the MPL. All the samples involved less concentrations of Zn than the MPL (5 $\mu\text{g/g}$).

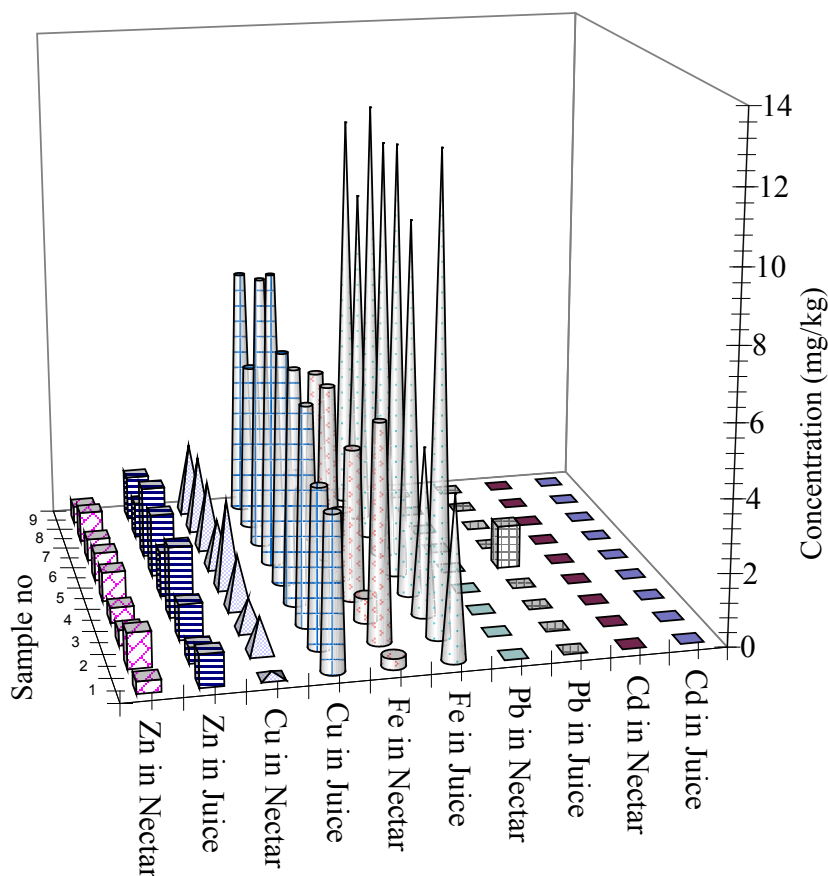


Figure 1. The Concentrations of Cd, Cu, Fe, Pb and Zn in Apple Juices and Nectars (mg/kg)

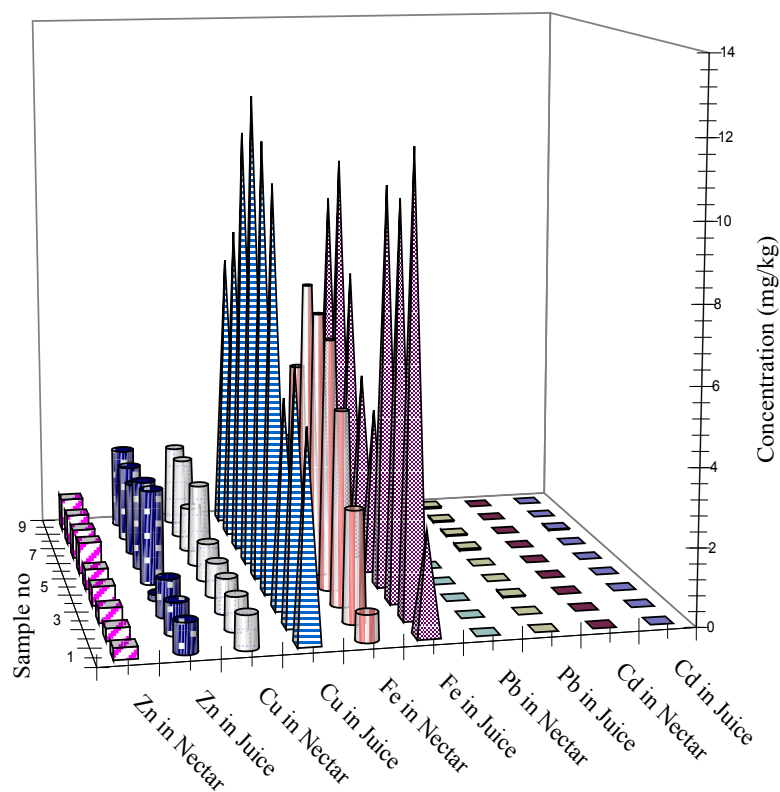


Figure 2. The Concentrations of Cd, Cu, Fe , Pb and Zn in Guava Juices and Nectars (mg/kg)

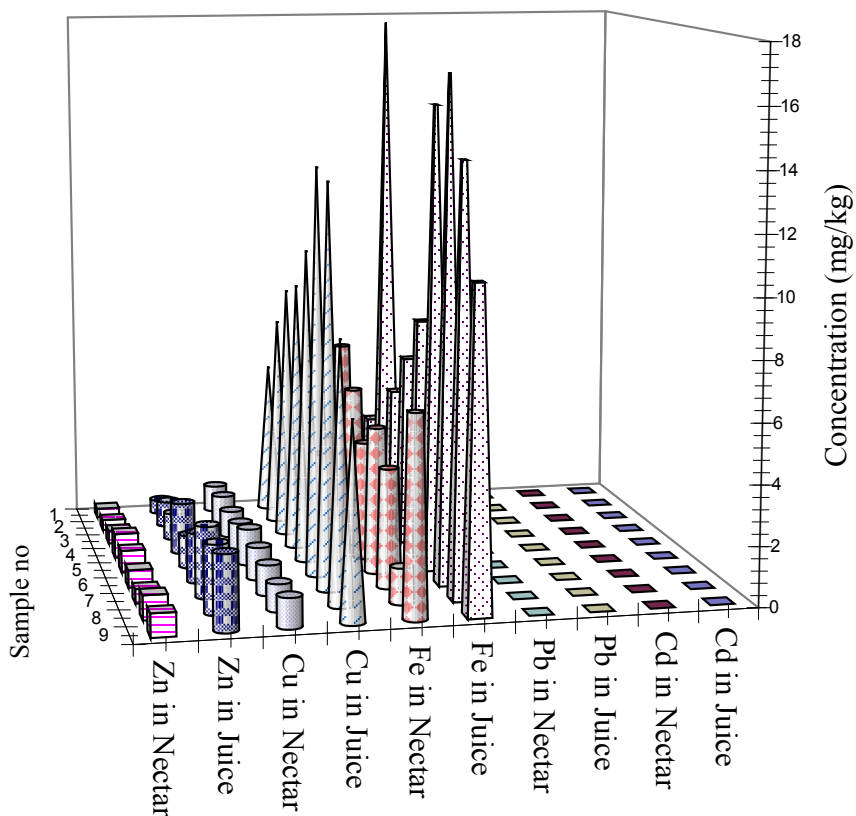


Figure 3. The Concentrations of Cd, Cu, Fe , Pb and Zn in Mango Juices and Nectars (mg/kg)

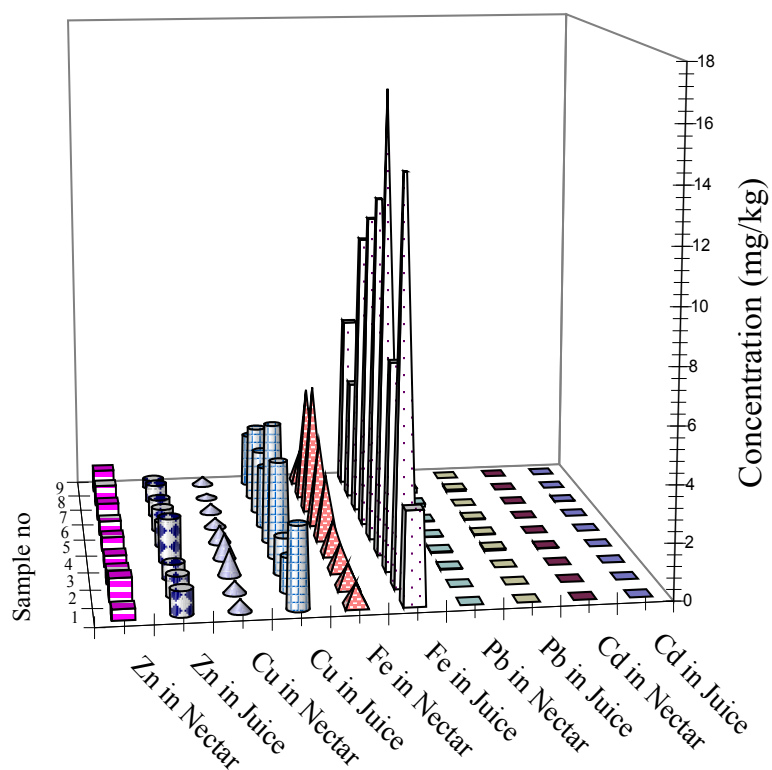


Figure 4. The Concentrations of Cd, Cu, Fe , Pb and Zn in Orange Juices and Nectars (mg/kg)

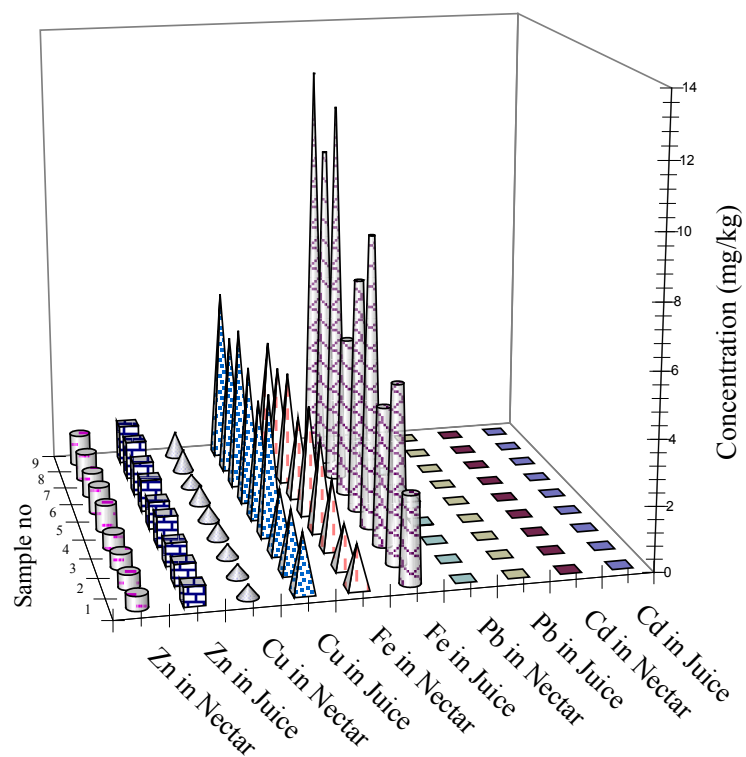


Figure 5. The Concentrations of Cd, Cu, Fe , Pb and Zn in Peach Juices and Nectars (mg/kg)

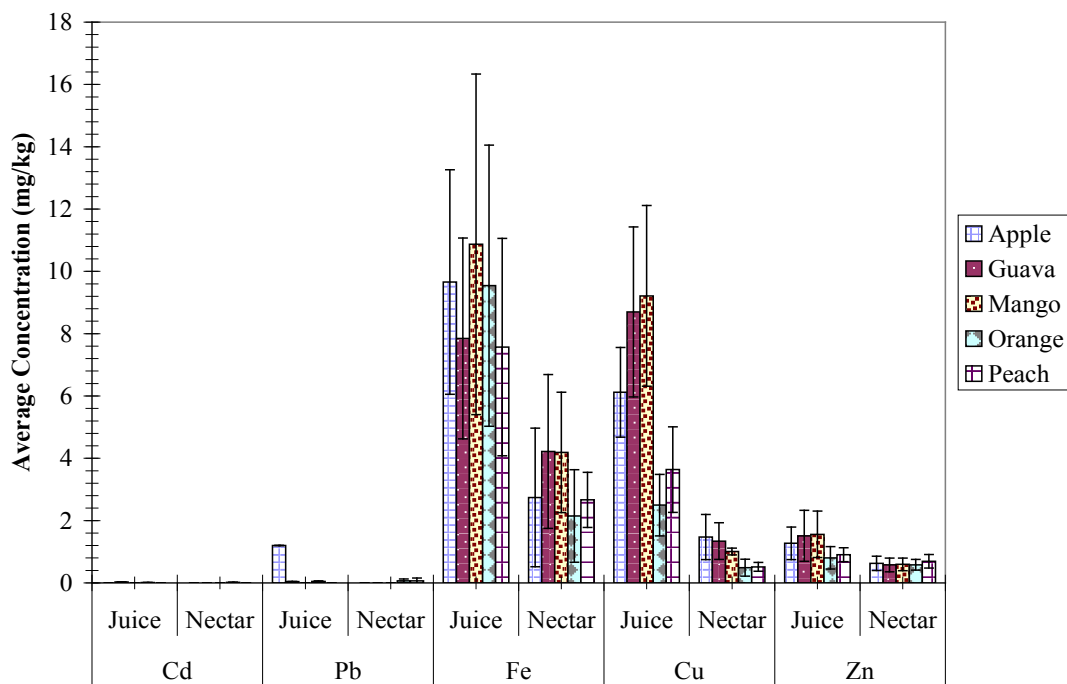


Figure 6. The Average Concentrations of Cd, Cu, Fe, Pb and Zn in Fruit Juices and Nectars \pm Standard Deviations (mg/kg)

From Figures 3 and 6 Fe in Mango juice was the highest among all data with 17.86 $\mu\text{g/g}$. The lowest Fe concentration (0.3 $\mu\text{g/g}$) was that in apple nectar. Copper ranged between 0.15 in apple nectar and 12.36 $\mu\text{g/g}$ in Guava juice. The maximum and minimum concentrations of Zn occurred in guava and mango juices (0.165 and 2.51 $\mu\text{g/g}$), respectively. The average concentrations of Fe ranged between 2.149 and 10.87 $\mu\text{g/g}$ in orange nectar and mango juice, respectively, while for Cu the case was that the mean was between 0.4889 $\mu\text{g/g}$ for orange nectar and 9.214 $\mu\text{g/g}$ for mango juice. The least results were for Zn with average range (0.5767 - 1.56 $\mu\text{g/g}$) for guava nectar and mango juice, respectively. A total of 33 juice and 7 nectar samples of 90 (71.1%, 15.6%, respectively) violating the Fe MPL. Twenty five juice samples of 45 (53.3%) violating the MPL of Cu. No nectar sample contains Cu more the than allowed limits. Neither juice nor nectar samples involved Zn concentrations violating the limits.

Statistically, the differences in the mean values among the five metals for each of the juices and nectars of the five fruits are greater than would be expected by chance; and therefore, there is a statistically significant difference ($P = <0.001$) with overall significance level = 0.05 using Holm-Sidak method. The differences in the mean values of each metal among the five fruit juice groups, do not exclude the possibility that the difference is due to random sampling selection, are not statistically significant ($P = 0.948, 0.984, 0.967, 0.967$ and 0.865 for Cd, Pb, Fe, Cu and Zn, respectively) between these different collection of fruit juice samples, the power of the performed test is 0.050.

The levels of some heavy metals in lime, lemon and orange fruit juice from the Abura - Asebu- Kwamankese

District of the Central Region of Ghana were determined [13]. The samples were analyzed for As, Pb, Cr, Ni, Fe, Zn and Cu using ICP-AES. Iron, zinc and lead were found in all the samples with mean concentrations respectively 1.2065, 2.401×10^{-1} and 2.92×10^{-2} $\mu\text{g/g}$. Copper was found in the lime only with concentrations 4.313×10^{-3} $\mu\text{g/g}$. These results are far different from ours. Misleading dependence of them is illogic. At least the results of essential metals are much higher than our ones. This could be due to different environmental condition of fruit cultivation and/or juice processing and packing. However, Krejpcio and Sionkowski studied the contents of Pb, Cd, Cu and Zn in fruit juices using atomic absorption spectrometry to determine the safety of some food available in the Polish market [14]. It was found that most fruit juice sample (88%) met the national standard criteria, but Pb and Cd exceeded the permissible limits for 3% and 9%, respectively. These data could have a point of resemblance with ours, although diverse criteria may be applied. However the use of the same technique of determination (AAS) with closer detection limits may be a reasonably worthwhile factor.

4. Conclusions

Although some of the samples showed concentrations within or below the maximum allowed limits, most samples had higher iron levels than the allowed limits, copper values were moderate but all sample zinc were lower than the MPL. Toxic metal Cd has lower results than the limits. Most Pb in the juice sample was lower than the allowed limits except four orange samples of, one apple juice sample and one peach nectar sample. These findings may be in accordance

with some ones and may contradict other authors. This may be due to different factors such as cultivation (soil, irrigation, atmosphere and weathering), juice processing and packing. From the statistical point of view, the difference between the values among the five metals for each of the juices and nectars of the five fruits was significant, but the differences in the mean values of each metal among the five fruit juice groups was not significant.

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