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Estimation of Toxic Metal Contamination Levels in Beverages Samples Collected from Lahore City in Pakistan.

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Abstract

The present study was conducted to evaluate the risk associated to human health by heavy metals through the intake of beverages (fruit juices, soft and energy drinks) excessively used in city Lahore, Pakistan. The concentration in ppm of heavy metals (Pb, Cr, Co, Cd, Zn and Ni) in 17 popular beverages has been investigated by using Flame Atomic Absorption Spectrophotometer (AAnalyst 400-PerkinElmer). A range of standard solutions were prepared according to the standard methods governed by American Public Health Association. It has been observed that concentration of some heavy metals (i.e. Pb, Cr, Co, Zn and Ni) in all collected samples (i.e. 17) were found close to the Standard permissible limits provided by Pakistan Standards Quality Control Authority (PSQCA). However, all samples were free from any detectable concentration levels of Cd.

***Keywords**: Toxic Metals, Processed Juices, Soft Drinks, Carbonated Drinks, Energy Drinks Pakistan*

1. Introduction:

Beverages (fruit juices, soft and energy drinks) have become an important necessity of modern diet in many countries. Beverages like fruit juices can play an important role in providing nutrients present naturally in fruits to human body and are available in natural concentrations as well as processed form [1]. These juices are healthy as they do not contain any fats and are enriched in vitamins, minerals and natural phytonutrients. Soft drinks are composed of water, Carbon dioxide, sweetener with mostly balanced acidity and it does not contain any alcoholic content [2]. As beverages are processed in industries so there can be multiple factors which could be a reason for heavy metal contamination. Most important source of heavy metal-contamination may include water used for their preparation as heavy metals accumulate in water supply from waste of industries, houses, lead pipes or from flavors, sugar mixture (molasses) because pesticides used in the fields of sugarcane could also contain heavy metals. Also, Acid rain results in the breakdown of soils and liberates heavy metals into rivers, groundwater etc.

Heavy metals are hazardous, because of bioaccumulation, which results from increase in amount of chemical in bio material with passage of time as compared to natural amount of chemicals in

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the environment [3]. Heavy metals are directly toxic to the humans and are non-degradable. Their vacant orbitals make bond with almost majority of the biological molecules which modulate their structure and function, resulting into major diseases i.e. cancer, neural disorder as well as cellular, tissue and organ damage [4-6]. The International Agency for Research has found that *Cd* is cancer causing. Pb is toxic and can affect nervous system and peripheral nervous system. The major targets of P*b* contamination are mostly young children. *Cd* is a collective nephron toxicant that is captivated into the body from food [7]. Toxicity of *Ni* increases the chances of lung cancer, nose cancer, larynx cancer, and also causes sickness and dizziness, lung embolism, respiratory failure, birth defects, asthma, chronic bronchitis and allergic reactions [8]. Fruit juices, soft and carbonated drinks are some of the most widespread beverages in the habitual diet and they can contribute intake of *Cr*, the poisoning of which can be chronic [7]. In many developing countries, *Zn* deficiency increases the risk of illness and death from infectious diseases in children [9]. *Co* is used to make thyroid hormone thyroxin and causes the red blood cells production. *Co* is less toxic as compared to other heavy metals [10]. Thus, quality of fruit juices is strictly upheld in urbanized countries under some rules and regulations but in many countries the industrialist is not worried about the microbiological safety and cleanliness of beverages because of carelessness of law. Thus, in recent years, beverages have become a major cause for the transfer of diseases in humans. This scenario needs proper analysis, standardization, and regulation of these industrial processes and their products for the toxic metal contents.

In order to develop awareness among the people about beverages in transmitting diseases, this study was conducted for the precise determination of the heavy metal concentrations i.e. *Pb, Cr, Co, Cd, Zn and Ni* of selected beverages available in Pakistan in Lahore city, during November 2016 and for comparison of these results with the standard permissible limits governed by different agencies: World Health Organizations [11], United Sates Environmental Protection Agency (US-EPA) [12], and Pakistan Standards Quality Control Authority [13] are provided in Table 1.

Table 1: Guidelines for drinking water governed by different organizations i.e. [1]World Health Organization (WHO) [11] , [2]United Sates Environmental Protection Agency (US-EPA) [12], [3]Pakistan Standards Quality Control Authority [13].

Sr.#	Metal	[11]WHO *SPL(mg/L)	[12]US *SPL(mg/L)	[13]PSQCA*SPL(mg/L)
1	Lead (Pb)	0.001	0	0.05
2	Chromium (Cr)	0.05	0.01	0.05
3	Cobalt (Co)	0.05	0.01	0.05
4	Cadmium (Cd)	0.003	0.005	0.01
5	Zinc (Zn)	----	5.00	5.00
6	Nickle (Ni)	0.02	-----	0.02

2. Experimental Work:

2.1. Collection And Preparation of samples

Seventeen flavors of beverages (processed juices, soft and energy drinks) were randomly purchased in November 2016, from different super stores/ public market in Lahore.

2.2. Sample preparation for the estimation of metals:

The standard samples have been prepared according to digestion procedure, which has been explained in literature [14]. The 10 mL of each beverage sample was pipetted out from the sealed bottle of respective beverage and transferred into 100 mL digestion flask. 5 mL of concentrated Nitric Acid (68-69%) was added into each digestion flask and heated till boiling then hydrogen peroxide (H_2O_2) was added dropwise, till the solution became colorless. Samples were cooled down and then total volume of each sample was increased up to 100 mL by adding distilled water.

2.3. Specification of Atomic Absorption Spectrophotometer (AAS):

Operating parameters of Atomic Absorption Spectrophotometer (Perkin Elmer AAnalyst 400) was used in the analysis of trace metals using respective wavelengths in the range of 189-900nm, Focal length: 300 mm., Grating: 36 x 185 mm area, 79 lines/mm, blaze angle 76?, Fused-quartz prism: 95 x 40 mm, 60°, Spectral bandpass: 0.15 nm at 200 nm, Reciprocal linear dispersion: 2.4 nm/mm. WinLab32™ (AAS software) was used to control all the functions of the AAnalyst™ 400 to automatically calculate the mean of three readings of three same samples of each product for each metal. The diagram of Atomic Absorption Spectrophotometer (AAS) is shown in (Fig. 1).

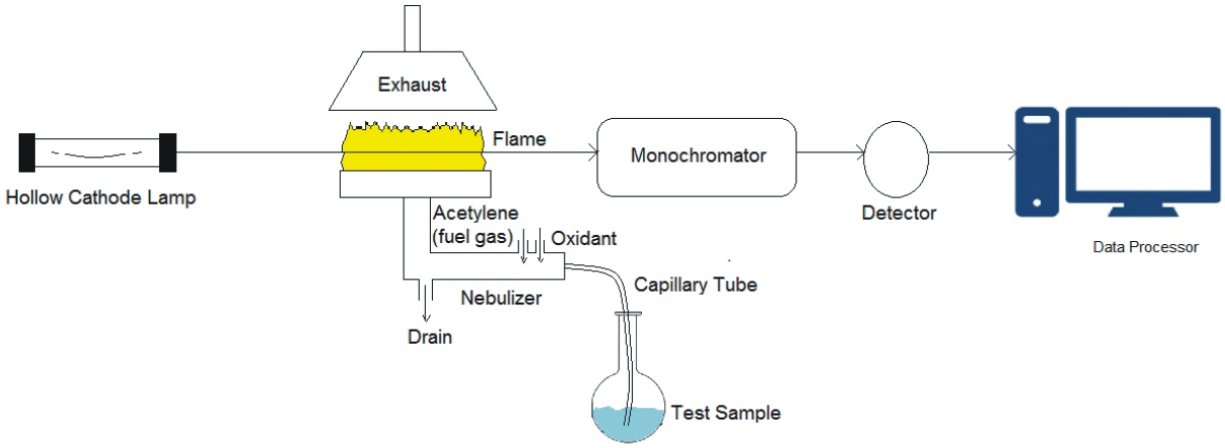

Figure 1: Diagram of Flame Atomic Absorption Spectrophotometer.

3. Results and Discussion:

The concentrations (mg/L) of Pb, Cr, Cd, Co, Zn and Ni present in 17 beverages in Lahore, Pakistan are shown in (Table 2 (a) and Table 2 (b)). The concentration level charts are shown in (Fig. 2 and 3). (Table 3) shows the amounts of heavy metals concentration in 17 samples of beverages in summarized form.

Table 2 (a): Mean value of heavy metal ionic concentration in beverages (processed juices, soft, carbonated and energy drinks)

Sr. No	Types of Drinks	Pb (mg/L)	Cr (mg/L)	Co (mg/L)	Cd (mg/L)	Zn (mg/L)	Ni (mg/L)
1	Fruit juice 1	0.039	0.033	0.076	0.000	0.114	0.016
		0.041	0.041	0.033	0.000	0.121	0.017
		0.034	0.043	0.034	0.000	0.107	0.013
	Mean	**0.0380**	**0.0390**	**0.0477**	**0.0000**	**0.1140**	**0.0153**
2	Fruit juice 2	0.015	0.036	0.044	0.000	0.033	0.015
		0.019	0.049	0.059	0.000	0.078	0.012
		0.010	0.042	0.047	0.000	0.078	0.020
	Mean	**0.0147**	**0.0423**	**0.0500**	**0.0000**	**0.0630**	**0.0157**
3	Fruit juice3	0.043	0.027	0.023	0.000	0.006	0.013
		0.039	0.026	0.026	0.000	0.023	0.013
		0.035	0.028	0.023	0.000	0.016	0.015
	Mean	**0.0390**	**0.0270**	**0.0240**	0.0000	**0.0150**	**0.0138**
4	Fruit juice 4	0.049	0.049	0.037	0.000	0.078	0.023
		0.056	0.049	0.038	0.000	0.098	0.013
		0.048	0.050	0.031	0.000	0.078	0.014
	Mean	**0.0507**	**0.0494**	**0.0353**	0.0000	**0.0847**	**0.0167**
5	Fruit juice 5	0.041	0.048	0.045	0.000	0.059	0.017
		0.046	0.043	0.026	0.000	0.050	0.013
		0.038	0.048	0.064	0.000	0.027	0.018
	Mean	**0.0417**	**0.0303**	**0.0450**	0.0000	**0.0453**	**0.0161**
6	Soft drink 1	0.020	0.020	0.034	0.000	0.361	0.022
		0.031	0.033	0.055	0.000	0.263	0.022
		0.029	0.029	0.061	0.000	0.247	0.012
	Mean	**0.0267**	**0.0273**	**0.0499**	**0.0000**	**0.2903**	**0.0187**
7	Soft drink 2	0.025	0.047	0.056	0.000	0.107	0.019
		0.029	0.048	0.051	0.000	0.131	0.020
		0.032	0.048	0.040	0.000	0.100	0.017
	Mean	**0.0287**	**0.0475**	**0.0490**	**0.0000**	**0.1127**	**0.0187**
8	Soft drink 3	0.029	0.027	0.048	0.000	0.126	0.016
		0.037	0.029	0.046	0.000	0.103	0.012
		0.033	0.023	0.057	0.000	0.118	0.011
	Mean	**0.0330**	**0.0264**	**0.0503**	**0.0000**	**0.1157**	**0.0129**
9	Soft drink 4	0.048	0.043	0.052	0.000	0.111	0.014
		0.041	0.052	0.055	0.000	0.133	0.011
		0.039	0.046	0.040	0.000	0.115	0.011
	Mean	**0.0427**	**0.0470**	**0.0490**	**0.0000**	**0.1197**	**0.0120**
10	Soft drink 5	0.013	0.046	0.060	0.000	0.044	0.018
		0.014	0.043	0.041	0.000	0.062	0.019
		0.019	0.035	0.049	0.000	0.038	0.019
	Mean	**0.0153**	**0.0412**	**0.0500**	**0.0000**	**0.0480**	**0.0189**

Table 2 (b): Mean value of heavy metal ionic concentration in beverages (processed juices, soft, carbonated and energy drinks)

Sr. No	Types of Drinks	Pb (mg/L)	Cr (mg/L)	Co (mg/L)	Cd (mg/L)	Zn (mg/L)	Ni (mg/L)
11	Soft drink 6	0.018	0.049	0.045	0.000	0.022	0.017
		0.018	0.045	0.052	0.000	0.054	0.019
		0.020	0.043	0.052	0.000	0.076	0.021
	Mean	**0.0187**	**0.0457**	**0.0497**	**0.0000**	**0.0507**	**0.0190**
12	Soft drink 7	0.029	0.046	0.043	0.000	0.049	0.014
		0.022	0.047	0.044	0.000	0.042	0.020
		0.025	0.049	0.055	0.000	0.055	0.023
	Mean	**0.0253**	**0.0471**	**0.0473**	**0.0000**	**0.0487**	**0.0190**
13	Soft drink 8	0.013	0.045	0.044	0.000	0.059	0.021
		0.010	0.050	0.040	0.000	0.049	0.020
		0.011	0.049	0.046	0.000	0.017	0.014
	Mean	**0.0113**	**0.0480**	**0.0433**	**0.0000**	**0.0417**	**0.0183**
14	Soft drink 9	0.047	0.037	0.043	0.000	0.016	0.023
		0.042	0.039	0.047	0.000	0.037	0.020
		0.040	0.042	0.038	0.000	0.300	0.014
	Mean	**0.0430**	**0.0392**	**0.0427**	0.0000	**0.1177**	**0.0190**
15	Soft drink 10	0.056	0.036	0.028	0.000	0.057	0.020
		0.046	0.045	0.055	0.000	0.040	0.013
		0.048	0.041	0.053	0.000	0.046	0.013
	Mean	**0.0501**	**0.0407**	**0.0453**	0.0000	**0.0477**	**0.0153**
16	Soft drink 11	0.046	0.036	0.045	0.000	0.046	0.019
		0.046	0.032	0.043	0.000	0.027	0.013
		0.047	0.046	0.039	0.000	0.025	0.018
	Mean	**0.0465**	**0.0380**	**0.0426**	0.0000	**0.0327**	**0.0167**
17	Energy drink	0.039	0.051	0.038	0.000	0.025	0.016
		0.059	0.052	0.053	0.000	0.030	0.013
		0.023	0.045	0.045	0.000	0.018	0.017
	Mean	**0.0407**	**0.0494**	**0.0453**	0.0000	**0.0243**	**0.0154**

Table 3: Heavy metal ionic concentrations in beverages (processed juices, soft and energy drinks)

Sr. No	Types of Drinks	Pb (mg/L)	Cr (mg/L)	Co (mg/L)	Cd (mg/L)	Zn (mg/L)	Ni (mg/L)
1	Fruit juice 1	0.0380	0.0390	0.0477	0.0000	0.1140	0.0153
2	Fruit juice 2	0.0147	0.0423	0.0500	0.0000	0.0630	0.0157
3	Fruit juice3	0.0390	0.0270	0.0240	0.0000	0.0150	0.0138
4	Fruit juice 4	0.0507	0.0494	0.0353	0.0000	0.0847	0.0167
5	Fruit juice 5	0.0417	0.0303	0.0450	0.0000	0.0453	0.0161
6	Soft drink 1	0.0267	0.0273	0.0499	0.0000	0.2903	0.0187
7	Soft drink 2	0.0287	0.0475	0.0490	0.0000	0.1127	0.0187
8	Soft drink 3	0.0330	0.0264	0.0503	0.0000	0.1157	0.0129
9	Soft drink 4	0.0427	0.0470	0.0490	0.0000	0.1197	0.0120
10	Soft drink 5	0.0153	0.0412	0.0500	0.0000	0.0480	0.0189
11	Soft drink 6	0.0187	0.0457	0.0497	0.0000	0.0507	0.0190
12	Soft drink 7	0.0253	0.0471	0.0473	0.0000	0.0487	0.0190
13	Soft drink 8	0.0113	0.0480	0.0433	0.0000	0.0417	0.0183
14	Soft drink 9	0.0430	0.0392	0.0427	0.0000	0.1177	0.0190
15	Soft drink 10	0.0501	0.0407	0.0453	0.0000	0.0477	0.0153
16	Soft drink 11	0.0465	0.0380	0.0426	0.0000	0.0327	0.0167
17	Energy drink 1	0.0407	0.0494	0.0453	0.0000	0.0243	0.0154

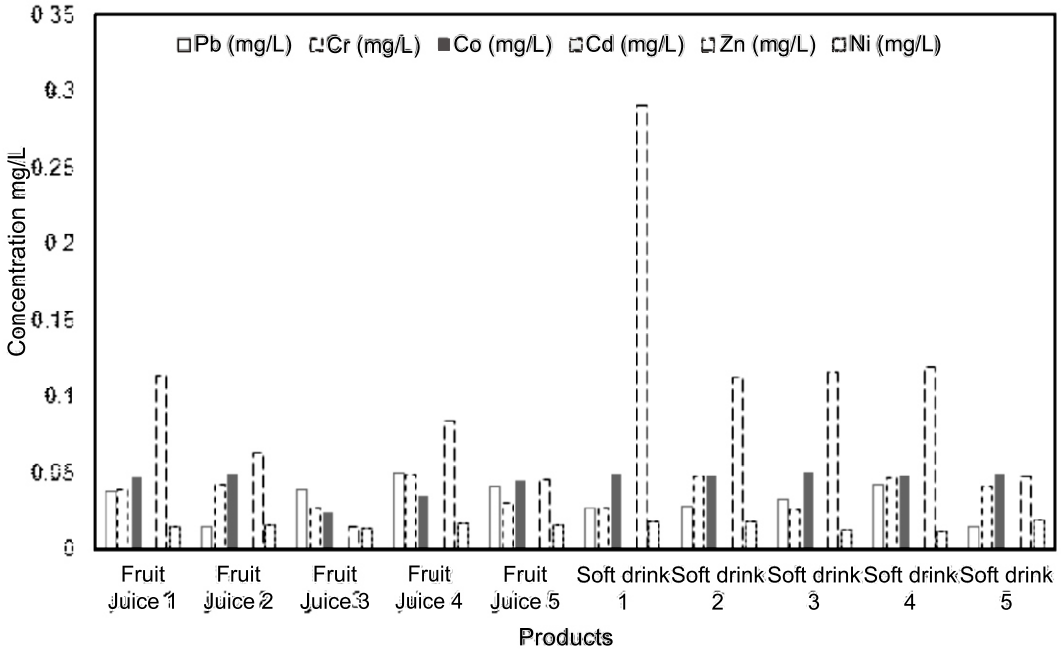

Figure 2: Comparison of heavy metal ionic concentration in beverages (mg/L).

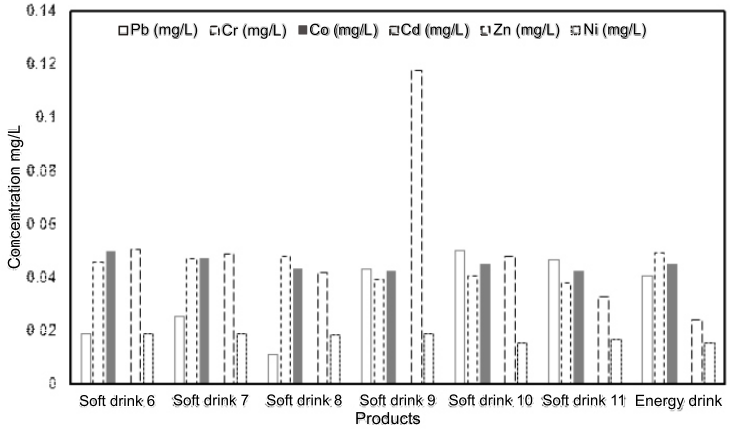

Figure 3: Comparison of heavy metal ionic concentration in beverages (mg/L).

The concentration of Pb and Cr in most of the beverages samples were found close to standard permissible limit (i.e. 0.05 mg/L for both) as provided by PSQCA [12]. However soft drink no. 10 (0.0501 mg/L) and fruit juice no. 4 (0.0507 mg/L) contain Pb slightly higher than the standard permissible limit. The maximum concentration of Cr was found in fruit juice no. 4 and energy drink no.1 i.e 0.0494 mg/L for both however it is lower than standard permissible limit i.e 0.05 mg/L. Pb and Cr concentration in 17 beverages samples are shown in (Fig. 4 and 5) respectively. All the samples analyzed were free from Cd. The Co was found in soft drink no. 3 (0.0503 mg/L), fruit juice no. 2 (0.0500 mg/L) and soft drink no. 5 (0.0500 mg/L). The Ni was found in soft drink no. 6 (0.019 mg/L), soft drink no. 7 (0.019 mg/L) and soft drink no. 9 (0.019 mg/L). The contents of Co and Ni in beverages samples were also low and did not reach the standard permissible limit (i.e. 0.05 mg/L for both Ni and Co). Co and Ni concentration in 17 beverages samples are shown in (Fig. 6 and 7) respectively. The concentration levels of Zn, the highest mean values of which was found in soft drink no. 1 and soft drink no. 2 i.e. (0.2903 mg/L) and (0.1197 mg/L) respectively whereas standard permissible limit for Zn is 5 mg/L. Zn concentration in 17 beverages samples is shown in (Fig. 8). The obtained results showed samples found contaminated with different level of concentrations majorly in standard permissible limits of heavy metals.

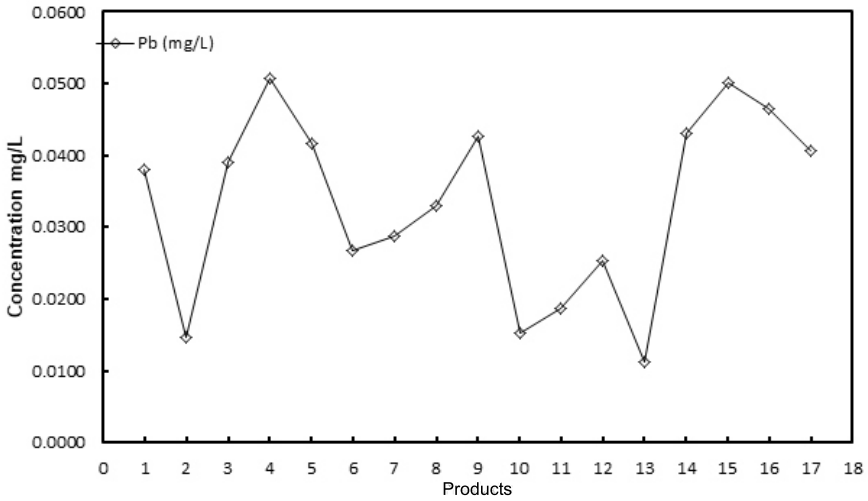

Figure 4: Lead (Pb) concentrations in selected products (mg/L) i.e 1. Fruit juice 1, 2. Fruit juice 2, 3. Fruit juice 3, 4. Fruit juice 4, 5. Fruit juice 5, 6. Soft drink 1, 7. Soft drink 2, 8. Soft drink 3, 9. Soft drink 4, 10. Soft drink 5, 11. Soft drink 6, 12. Soft drink 7, 13. Soft drink 8, 14. Soft drink 9, 15. Soft drink 10, 16. Soft drink 11, 17. Energy Drink

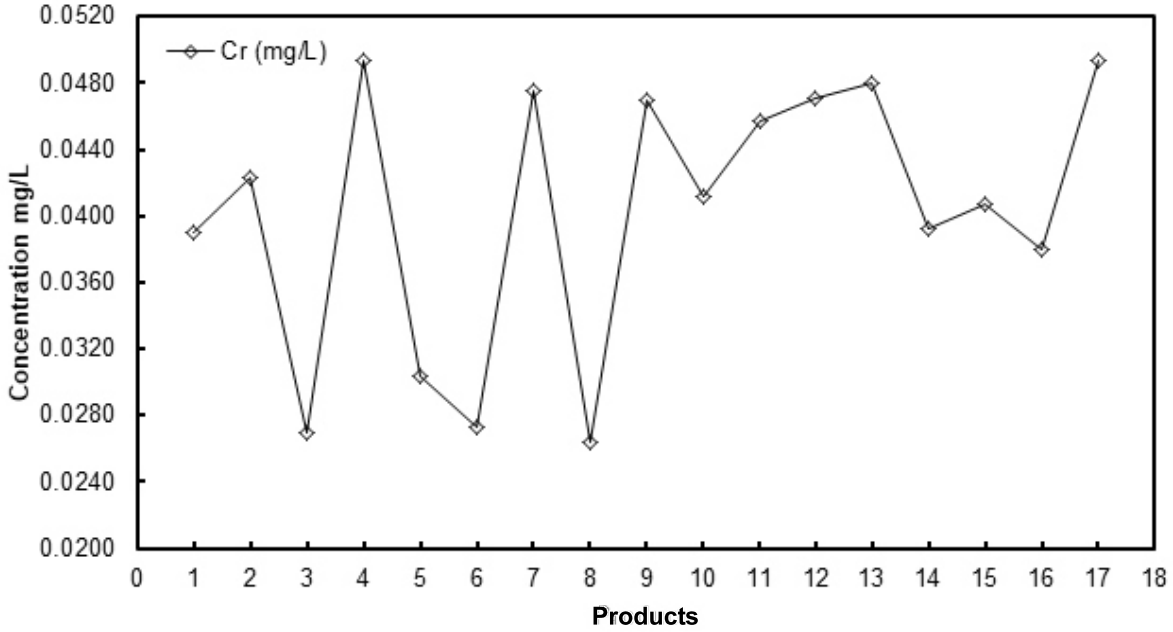

Figure 5: Chromium (Cr) concentrations in selected products (mg/L) i.e 1. Fruit juice 1, 2. Fruit juice 2, 3. Fruit juice 3, 4. Fruit juice 4, 5. Fruit juice 5, 6. Soft drink 1, 7. Soft drink 2, 8. Soft drink 3, 9. Soft drink 4, 10. Soft drink 5, 11. Soft drink 6, 12. Soft drink 7, 13. Soft drink 8, 14. Soft drink 9, 15. Soft drink 10, 16. Soft drink 11, 17. Energy Drink

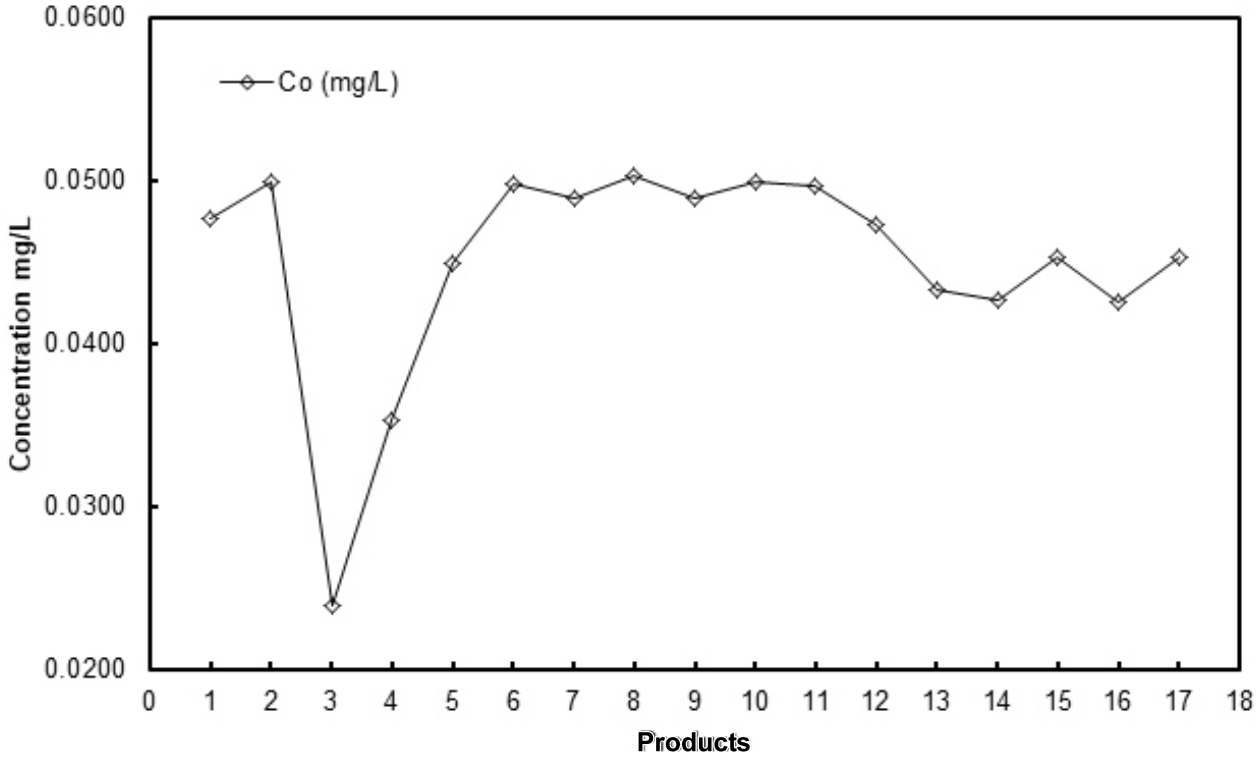

Figure 6: Cobalt (Co) concentrations in selected products (mg/L) i.e 1. Fruit juice 1, 2. Fruit juice 2, 3. Fruit juice 3, 4. Fruit juice 4, 5. Fruit juice 5, 6. Soft drink 1, 7. Soft drink 2, 8. Soft drink 3, 9. Soft drink 4, 10. Soft drink 5, 11. Soft drink 6, 12. Soft drink 7, 13. Soft drink 8, 14. Soft drink 9, 15. Soft drink 10, 16. Soft drink 11, 17. Energy Drink

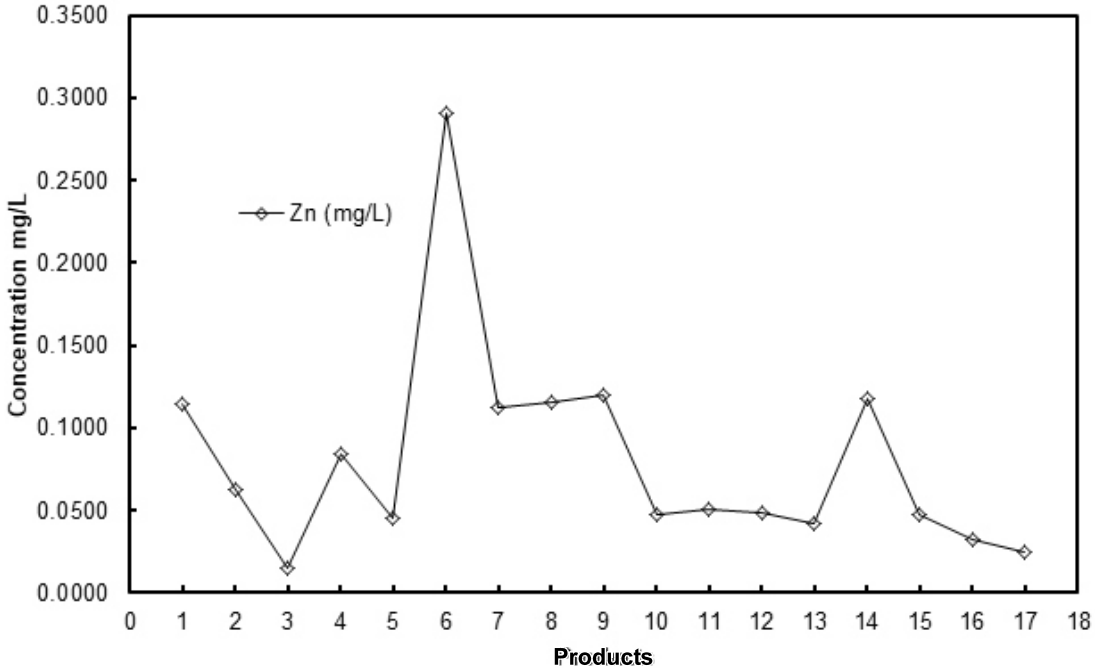

Figure 7: Zinc (Zn) concentrations in selected products (mg/L) i. 1. Fruit juice 1, 2. Fruit juice 2, 3. Fruit juice 3, 4. Fruit juice 4, 5. Fruit juice 5, 6. Soft drink 1, 7. Soft drink 2, 8. Soft drink 3, 9. Soft drink 4, 10. Soft drink 5, 11. Soft drink 6, 12. Soft drink 7, 13. Soft drink 8, 14. Soft drink 9, 15. Soft drink 10, 16. Soft drink 11, 17. Energy Drink

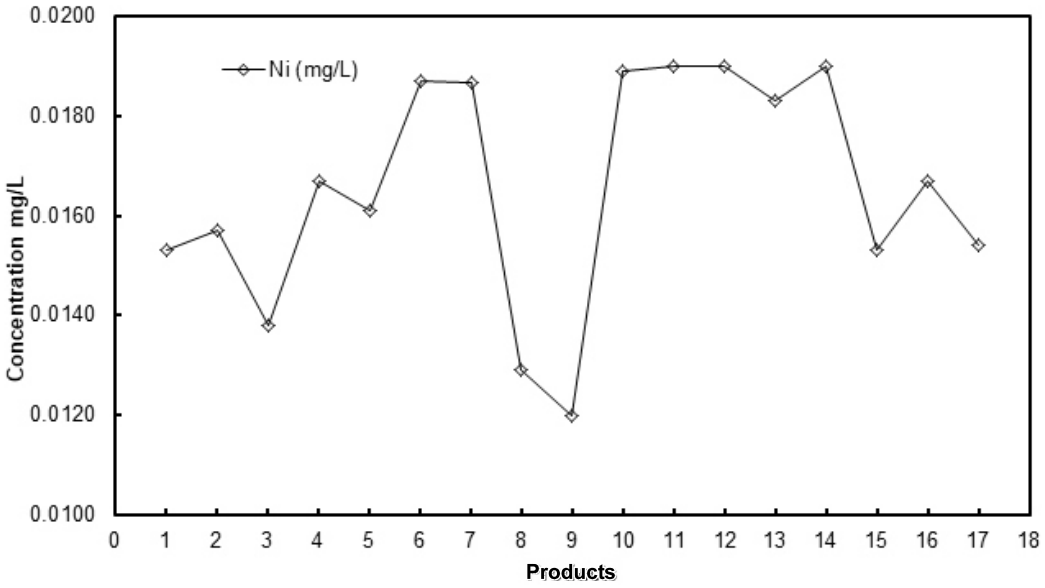

Figure 8: Nickel (Ni) concentrations in selected products (mg/L) i.e 1. Fruit juice 1, 2. Fruit juice 2, 3. Fruit juice 3, 4. Fruit juice 4, 5. Fruit juice 5, 6. Soft drink 1, 7. Soft drink 2, 8. Soft drink 3, 9. Soft drink 4, 10. Soft drink 5, 11. Soft drink 6, 12. Soft drink 7, 13. Soft drink 8, 14. Soft drink 9, 15. Soft drink 10, 16. Soft drink 11, 17. Energy Drink

The content of heavy metals found in beverages was relatively low and did not reach the upper permissible limit in most of the beverages. It was found that most beverages samples met the national standard criteria. The lower heavy metal concentrations observed for these samples could arise from contamination either from the processing step or from an existing contamination in the drinking water used in beverages processing.

4. Conclusions:

In this study all available beverages samples from Lahore city, has been analyzed for the detection of Pb, Cr, Cd, Co, Zn and Ni. In most of the beverages the level of Pb, Cr, Co, Zn and Ni concentrations were found close to the upper standard permissible limits provided by Pakistan Standards Quality Control Authority (PSQCA, 2008). It is concluded that all beverages samples were free from any detectable concentration levels of Cd. However, soft drink no. 10 (0.0501 mg/L) and fruit juice no. 4 (0.0507 mg/L) contains Pb slightly higher than the standard permissible limit i.e. (0.05 mg/L). The soft drink no. 3 (0.0503 mg/L), fruit juice no. 2 (0.0500 mg/L) and soft drink no. 5 (0.0500 mg/L) contains Co slightly higher than the standard permissible limit i.e. (0.05 mg/L) as provided by Pakistan Standards Quality Control Authority (PSQCA, 2008).

References:

1. Tasnim, F., Quality assessment of industrially processed fruit juices available in dhaka city, bangladesh. Malaysian journal of nutrition, 2010. 16(3).
2. Ofori, H., M. Owusu, and G. Anyebuno, Heavy metal analysis of fruit juice and soft drinks bought from retail market in Accra, Ghana. 2013.
3. Eyong, E., M. Eteng, and U. Eyong, Comparative chemical analysis of some brand of soft drinks consumed in Southern Nigeria. Nig. J. Biochem. Mol. Biol, 2010. 25: p. 36-39.
4. Nessa, F. and S.A. Khan, Evaluation of Free Radical Scavenging Activity and Toxic Heavy Metal Contents of Commercially Available Fruits of Tribulus terrestris Linn. European J Med Plants, 2015. 9(3): p. 1-14.
5. Jomova, K. and M. Valko, Advances in metal-induced oxidative stress and human disease. Toxicology, 2011. 283(2): p. 65-87.
6. Singh, A., Health risk assessment of heavy metals via dietary intake of foodstuffs from the wastewater irrigated site of a dry tropical area of India. Food and Chemical Toxicology, 2010. 48(2): p. 611-619.
7. Maduabuchi, J.-M., Lead and cadmium exposures from canned and non-canned beverages in Nigeria: A public health concern. Science of the Total Environment, 2006. 366(2): p. 621-626.
8. Kasprzak, K.S., F.W. Sunderman, and K. Salnikow, Nickel carcinogenesis. Mutation Research/Fundamental and Molecular Mechanisms of Mutagenesis, 2003. 533(1): p. 67-97.
9. Black, R.E., Zinc deficiency, infectious disease and mortality in the developing world. The Journal of nutrition, 2003. 133(5): p. 1485S-1489S.
10. Song, K., Determination of trace cobalt in fruit samples by resonance ionization mass spectrometry. Microchemical Journal, 2003. 75(2): p. 87-96.
11. Organization, W.H., Guidelines for drinking-water quality: recommendations. Vol. 1. 2004: World Health Organization.
12. Talmage, S.S., Nitroaromatic munition compounds: environmental effects and screening values, in Reviews of environmental contamination and toxicology. 1999, Springer. p. 1-156.
13. Pak, E., National standards for drinking water quality. Pakistan Environmental Protection Agency, (Ministry of Environment) Government of Pakistan, 2008.
14. Association, A.P.H., Standard methods for the examination of water and wastewater. Vol. 1915: American Public Health Association.