

Concentrations of toxic heavy metals in coffee

Running title: Toxic Heavy Metals in Coffee

Abstracts:

Background and Objective

Coffees one of the common drinks in Middle Eastern countries including Saudi Arabia due to its desirable aroma, taste and putative positive physiological functions. The concentration of metals commonly present in coffee powder. The presence of heavy metal concentration in different brands of coffee powder available in Saudi Arabia market has been analyzed.

Methods

Thirteen different coffees brands were selected in different markets, all assessment was carried out in advanced instruments such as Inductively Coupled Plasma and Atomic Absorption Spectroscopy. There are 14 metals which divide into seven non toxic and seven toxic metals were analyzed. Non toxic metals are magnesium (Mg), calcium (Ca), Potassium (K), sodium (Na), phosphorus (P), iron (Fe), and toxic metals are arsenic (Ar), zinc (Zn), chromium (Cr), nickel (Ni), lead (Pb), antimony and cadmium (Cd)) these metals were direct and indirect effect on the human and environmental health.

Results

The mean and standard deviation of non-toxic and toxic metals concentration in different samples of coffee were as follows: Ca, Fe, K, Mg, Mn, Mo, Na were 24.873 ± 6.76 , 6.670 ± 4.88 , 235.985 ± 100.05 , 407.024 ± 226.56 , 8.637 ± 10.14 , 0.014 ± 0.01 , 333.865 ± 247.35 , 0.271 ± 0.22 , 0.939 ± 0.36 respectively. Toxic metals concentration were as Al, Cd, Cu, Ni, Pb, Si, Zn were

11.040±10.03, 0.802 ±2.52, 2.436±3.02, 0.072±0.110, 7.571±9.266, 23.480±27.32 and 1.853±1.66 respectively. These concentration values were high compared to TLVs of metals.

Conclusion

It was concluded from the study that coffee powder had high concentration of heavy toxic metals which is the major public health problem. Thus, quality control for food safety recommended during production of coffee.

Keywords; Coffee; daily intake; concentration; metals, toxic

Introduction

Coffee originates from the plant *Camellia sinensis*, a tree that may grow up to 52 feet in height unless cultivated.[1] Tea plants require significant rainfall of 50 inches a year and grow in acidic soil. Contaminants may vary in the soil, air, or water in which the plants are grown. Acidic soil may result in excess available aluminum and fluoride [1]. An acid or alkali soil pH also enhances leaching of toxic heavy metals from the soil [2]. Increasing pH with soluble calcium would reduce the absorption of fluoride [1]. Environmental pollutants such as fluoride and aluminum have been found in tea in part due to the tea plants absorption and deposition and concentration of these compounds in the leaves [3]. The drinking of more than 5 liters of tea per week may result in dental or skeletal fluorosis [4]. Mercury, lead, arsenic, and cadmium as well as other toxic elements have been found in tea leaves as described in the literature [5, 6]. Lead, arsenic, and cadmium have also been found in brewed black tea [7]. These soil and air contaminants may be directly related to the use of coal fired power plants.[8]

There is an abundance of literature demonstrating the adverse health effects of various heavy metal and metalloid elements on the human organism. By numerous mechanisms, including endocrine disruption [10], cytotoxicity [11], mitochondrial dysfunction [12], and oxidative stress [13- 14], a spectrum of toxic elements is able to disturb cellular and metabolic homeostasis and induce clinical illness. The literature is replete with many common disease processes such as carcinogenesis [15], insulin resistance [16],

neurodegeneration [17], and immune dysregulation [18-19]. Rather than isolated incidents of single exposures, it is apparent that toxic metal contact is a widespread phenomenon [20] with many potential sources including tainted food and drink, contaminated skin products, and contaminated air. Many toxic metals such as cadmium and lead have very long half-lives and thus are classified as persistent toxicants [21]. As some toxic elements appear to persist because of enterohepatic recycling [22, 23], even smaller levels of exposure can bioaccumulate and effect long-term harm.

The toxic elements such as lead, mercury, aluminum, and cadmium. The extremely low levels of lead accepted in Proposition 65 during the prenatal period come from our knowledge of the accumulation in the brain and resultant impairment of cognitive development [24-25].

Most evidence on the relation between coffee and blood pressure stems from cross-sectional studies. This evidence, however, is inconsistent. Some of these studies showed a positive relation (27), no relation (28), or even an inverse relation (29). Such cross-sectional studies have important limitations with respect to causal inference.

In Saudi Arabia, different brands of coffee available and coffee is one of the most common drink in the population. All the coffee beans were imported from different countries except the Arabic coffee. There is no previous study to determine the concentration of heavy metals in different brands of coffee which is the knowledge gap, this study results will help the food administration authority to check the all brands of coffee for heavy metals concentration and it also help the awareness among community for health conscious regarding coffee consumptions. The objective of study to determine the concentration of heavy metals present in different brands of coffee in Saudi Arabia market.

4. Material and Methods

Sampling method and Study setting

Coffees samples were taken from different markets in city of Damamm and Khobar and analyzed for heavy metal content using Inductive Couple Plasma OES. There are total 13 different types of coffees with different colors were selected through random sampling method.

Sample Preparation (Experiment)

After collection of Samples were collected by using stratified random methods. All the samples were in the form of powder. First sample was dried before the measurement of metals. Standard solutions were prepared according to the Shimadzu Perkin Elmer Pure Atomic Spectroscopy Standards guidelines (NIST traceable CRM, Perkin Elmer Corporation, USA and Merck □ Germany). Working standard solutions were prepared by diluting the stock solution with 0.1 M nitric acid for checking the linearity. The final residue was dissolved in 0.1 M HNO₃ solution and make up to 50 ml.

The glassware and polyethylene containers used for analysis. First washed with tap water, then soaked overnight in 6N HNO₃ solution and rinsed several times with ultrapure water to eliminate absorbance due to detergent. Accurately weighed (1 g) plant samples were transferred into a silica crucible and kept in a muffle furnace for ashing at 450

Analytical Procedure for coffee:

One gram (1gm) coffee samples were digested using 12cm³ of a mixture 5ml v/v) of concentrated HCl and HNO₃ acids. Analar grade reagents were used for the preparation of the standard solutions of these metals using their nitrate salts (Ca, K, Na Mg, Mn, Pb, Cu, Fe, Na, K and Zn) The diluted digests were analyzed by using Inductively Coupled Plasma (ICP-OES) was used for Mg, Mn, Ca, Pb, Cu, Fe and Zn. The metal concentrations in the coffee samples were read from standard curves by extrapolation. Also, the soluble samples of coffees were diluted and determine the physic and chemical parameters and compare between the two types of samples according to trace elements and physical constituents so the determination of physic- chemical characteristics and parameters of preserving teas and coffees in two

steps and these parameters which are used for soluble coffees according to its high degree of solubility such as

1- The physical parameters: such as pH, Conductivity, TDS, and temperature.

2- The chemical parameters: Ammonia, Nitrate, Nitrite, Sulfate, Sulfide, and Phosphate,

So, the determination of physic- chemical characteristics and parameters of preserving coffees in two steps and these parameters which are used for soluble coffees according to its high degree of solubility such as physic and chemical analysis for samples solutions according to the following table:

1- The physical parameters:

No	Parameters	Unit	Instrument	References
1	pH	-----	pH meter (electrode method)	Standard Method for the Examination of water and wastewater
2	Conductivity	ms/cm	Conductivity meter (electrode method)	
3	TDS	mg/L	Conductivity meter (electrode method)	
4	Temperature	°T	pH meter (electrode method)	

2- The chemical parameters:

No	Parameters	Unit	Instrument	References
1	Ammonia	mg/L	Spectrophotometer (HACH)	Standard Method for the Examination of water and wastewater
2	Nitrate	mg/L		
3	Nitrite	mg/L		
4	Sulfate	mg/L		
5	Sulfide	mg/L		
6	Phosphate	mg/L		
7	Total trace elements	ppm	ICP-OES and AAS	

Toxic Limit and Safe intake of heavy metals

<u>Heavy Metal</u>	<u>Toxic Limit</u>	<u>Recommended intake/Safe intake</u>
<u>Arsenic</u>	3 mg/day	15 - 25 µg/day
<u>Cadmium</u>	200 µg/kg	15 -50 µg/day
<u>Lead</u>	> 500 µg/L	20 - 280 µg/day
<u>Zinc</u>	150 µg/day	15µg/day

5. Results:

A- Physical and chemical analysis:

The mean values of samples as Ph 4.68 with SD0.57, conductivity 0.85, TDS 419.92, temperature 19.58 C, sulfate concentration 25, phosphate 40.3, ammonia 3.07, Nitrate 45.53.(Table 1)

B- Heavy metals:

Nontoxic heavy metals concentrations in different coffee samples

- Concentration levels of non-toxic metals: The average level concentration of calcium was ranged between 8.94 and 32.09 mg/kg, Iron was ranged between 1.27 and 14.35mg/kg, potassium was ranged between 21.31 and 306.71mg/kg, magnesium was ranged between 43.18 and 767.62mg/kg, manganese was ranged between 0.702 and 24.35 mg/kg, sodium was ranged between 6.84 and 556.5 mg/kg, copper was ranged between 0.133and 4.06 mg/kg, and zinc was ranged between 0.153 and 3.83 mg/kg, (Table 2)

Toxic heavy metals concentrations in different coffees samples

- Concentration levels of toxic metals: silver was ranged between 0 and 2.423 mg/kg, aluminum was ranged between 0.82 and 31.76 mg/kg, arsenic was ranged between 0 and 0.107 mg/kg, cadmium was ranged between 0 and 0.011, chromium was ranged between 0.0225 and 1.19, nickel was ranged between 0 and 0.258, lead was ranged between 0 and 21.45 mg/kg and antimony was ranged between 0.0086 and 0.133 mg/kg (Table 3)

Discussion:

Results of the study found that toxic heavy metal concentration were high in different brands of Coffee .these metals were hazards to various health effects on human body.

The different metals were found high concentration in different samples of coffee. The reason for this high concentration is that the soil where coffee plant grow and environmental conditions which effect the concentration. [30-32]. There are different factors which effect the concentration such as fertilizer used with different chemical compositions, coffee species and fertilized land where crop were grow. [33-34]. Previous studies found that the metal concentrations in coffee beans are important indicator to differentiated between different coffee variety.[35-36]

The pH of a coffee has been found to correlate with the perceived acidity in coffee and that is resulted in correlation between pH values and type of coffees. The pH values were ranged between 3.81 to 5.42 it is highly acidic in some samples that may lead to affecting on digestion of the food and performance of stomach. This result is consistent with the previous study [37]which showed that pH values ranges between 2-4 which is acidic in nature that affected the digestion problem and may lead to stomach cancer. It is well known throughout the coffees industry that decaffeinated coffee is more acidic than regular coffee due to the fact that decaffeinated coffee is made from Robusta beans. Robusta beans have a higher concentration of caffeine and more acidic than other beans. This is problematic for people with health problems such as acid reflux, GERDS and ulcers making them susceptible to detrimental effect of high levels of acidity also we found that there are variation in concentration of total dissolved solids.

According to the correlation between the heavy metals and types of coffees in the study results shows that some heavy metals were high concentrations of metals such as Ca, Fe, K, Mg, Mn and Na. The maximum concentrations of Ca was 32.09, Fe concentration (mg/kg) the maximum was 14.357, the third metals K concentration (mg/kg) the maximum concentration was 427.84. These results were consistent with other previous studies results which showed that these metals concentrations were high.[38]

Toxic heavy metals such as Al, As, Cd, Cr, Ni, Pb, Sb, and As also found high in the study results such as Al concentration (mg/kg) the maximum concentration was 31.769, As concentration (mg/kg) the maximum concentration was 0.107 Cd concentration (gm/kg) the maximum concentration was 0.0119, Cr

concentration (mg/kg) the maximum concentration was 1.1997. These results also consistent with other study results in which the concentration these toxic metals were found high.[39]

7. Conclusion:

The study result found that significant concentration of toxic heavy metals present in all samples of coffee which are hazardous to human health. There is need to develop the health promotion programme for awareness among community.

Declaration

Ethical approval and Consent to Participate

Study was approved by the hospital ethical committee with reference no is 287659 and consent of participate was obtained from the study participant.

All procedures performed in studies involving human participants were in accordance with the ethical standards of the institutional and/or national research committee and with the 1964 Helsinki declaration and its later amendments or comparable ethical standards. Research involve human participants, research approved from ethical review committee from hospital, confidentiality of data has maintained,

Informed consent inform consent was obtained from each participant

Consent for Publication

Informed written consent was received for publication of the manuscript and figure. Authors give permission to journal for publication

Availability of Data and Material

Data is confidential and not shared

8. References:

1. Wagesho, Y.; Chandravanshi, B.S. Levels of essential and non-essential metals in ginger (*Zingiber officinale*) cultivated in Ethiopia. *Springer Plus*, 2015, 4, Article No. 127. DOI: 10.1186/s40064-015-0899-5
2. Hiroyuki, K.T., Kazunobu, S., Takeji, T. (2011). Analysis of Iodinelike (Chlorine) Flavor-causing Components in Brazilian Coffee with Rio Flavor. *Food Sci. Technol. Res* 17(4): 347 – 352.
3. Ostrowska J., Stankiewicz A., Skrzydlewska E., Antioxidant properties of green tea. *Bromotol. Toxicol. Chem.* 2001; 2: 131.
4. Chandra S., De Mejia Gonzalez E., Polyphenolic compounds, antioxidant capacity, and quinone reductase activity of an aqueous extract of *Ardisia compressa* in comparison to mate (*Ilex paraguariensis*) and green (*Camellia sinensis*) teas. *J. Agric. Food Chem.* 2004; 52: 3583-3589.
5. Maron D. J., Lu G. P., Cai N. S., Wu Z. G., Li Y. H., Chen H., Zhu J. Q., Jin X., J., Wouters B. C., Zhao J., Cholesterol-lowering effect of a theaflavin-enriched green tea extract: a randomized controlled trial. *Arch. Intern. Med.* 2003; 163: 1448- 1453.
6. Hasegawa R., Chujo T., Sai-Kato K., Umemura T., Tanimura A., Kurokawa Y., Preventive effects of green tea against liver oxidative DNA damage and hepatotoxicity in rats treated with 2-nitropropane. *Food Chem. Toxicol.* 1995; 33: 961-970.
7. Fujiki H. Green tea: health benefits as cancer preventive for humans. *Chem. Rec.* 2005; 5: 119-132.
8. Bettuzzi S., Brausi M., Rizzi F., Castagnetti G., Peracchia G., Corti A., Chemoprevention of human prostate cancer by oral administration of green tea catechins in volunteers with high-grade prostate intraepithelial neoplasia: a preliminary report from a one-year proof-of-principle study. *Cancer Res.* 2006; 66: 1234-1240.
9. Seenivasan S., Manikandan N., Muraleedharan N.N., Selvasundaram R., Heavy metal content of black teas from south India, *Food Control.* 2008; 19: 746-749.
10. E. Álvarez-Ayuso, A. Giménez, and J. C. Ballesteros, “Fluoride accumulation by plants grown in acid soils amended with flue gas desulphurisation gypsum,” *Journal of Hazardous Materials*, vol. 192, no. 3, pp. 1659–1666, 2011.
11. Z. Tan and G. Xiao, “Leaching characteristics of fly ash from Chinese medical waste incineration,” *Waste Management and Research*, vol. 30, no. 3, pp. 285–294, 2012.
12. M. Fujimaki Hayacibara, C. S. Queiroz, C. P. Machado Tabchoury, and J. Aparecido Cury, “Fluoride and aluminum in teas and tea-based beverages,” *Revista de Saude Publica*, vol. 38, no. 1, pp. 100–105, 2004.

13. S.-C. C. Lung, H.-W. Cheng, and C. B. Fu, "Potential exposure and risk of fluoride intakes from tea drinks produced in Taiwan," *Journal of Exposure Science and Environmental Epidemiology*, vol. 18, no. 2, pp. 158–166, 2008.
14. X.-P. Wang, Y.-J. Ma, and Y.-C. Xu, "Studies on contents of arsenic, selenium, mercury and bismuth in tea samples collected from different regions by atomic fluorescence spectrometry," *Guang Pu Xue Yu Guang Pu Fen Xi*, vol. 28, no. 7, pp. 1653–1657, 2008.
15. W.-Y. Han, F.-J. Zhao, Y.-Z. Shi, L.-F. Ma, and J.-Y. Ruan, "Scale and causes of lead contamination in Chinese tea," *Environmental Pollution*, vol. 139, no. 1, pp. 125–132, 2006. .
16. Shekoohiyan, M. Ghoochani, A. Mohagheghian, A. H. Mahvi, M. Yunesian, and S. Nazmara, "Determination of lead, cadmium and arsenic in infusion tea cultivated in north of Iran," *Iranian Journal of Environmental Health Science & Engineering*, vol. 9, article 37, 2012.
17. D. Tang, T.-Y. Li, J. J. Liu et al., "Effects of prenatal exposure to coal-burning pollutants on children's development in China," *Environmental Health Perspectives*, vol. 116, no. 5, pp. 674–679, 2008.
18. M. E. Sears and S. J. Genus, "Environmental determinants of chronic disease and medical approaches: recognition, avoidance, supportive therapy, and detoxification," *Journal of Environmental and Public Health*, vol. 2012, Article ID 356798, 15 pages, 2012.
19. T. I. Lidsky and J. S. Schneider, "Lead neurotoxicity in children: basic mechanisms and clinical correlates," *Brain*, vol. 126, no. 1, pp. 5–19, 2003.
20. S. J. Genus, G. Schwalfenberg, A. K. Siy, and I. Rodushkin, "Toxic element contamination of natural health products and pharmaceutical preparations," *PLoS One*, vol. 7, no. 11, Article ID e49676, 2012.
21. M. A. Rahman, B. Rahman, and N. Ahmed, "High blood manganese in iron-deficient children in Karachi," *Public Health Nutrition*, vol. 16, no. 9, pp. 1677–1683, 2013. View at Publisher · View at Google Scholar
22. F. M. Crinella, "Does soy-based infant formula cause ADHD? Update and public policy considerations," *Expert Review of Neurotherapeutics*, vol. 12, no. 4, pp. 395–407, 2012. View at Publisher ·
23. Klag MJ, Wang NY, Meoni LA, et al. Coffee intake and risk of hypertension. The Johns Hopkins Precursors Study. *Arch Intern Med* 2002;162:657–62.
24. Ramato Ashu and Bhagwan Singh Chandravanshi, "CONCENTRATION LEVELS OF METALS IN COMMERCIALY AVAILABLE ETHIOPIAN ROASTED COFFEE POWDERS AND THEIR INFUSIONS" *Bull. Chem. Soc. Ethiop.* 2011, 25(1), 11-24.

25. Grembecka, M.; Malinowska, E.; Szefer, P. " Differentiation of market coffee and its infusions in view of their mineral composition" *Sci. Total Environ.* 2007, 383, 59.
26. Santos, E.E.; Lauria, D.C.; Porto da Silveira, C.L. " Assessment of daily intake of trace elements due to consumption of foodstuffs by adult inhabitants of Rio de Janeiro city" *Sci. Total Environ.* 2004, 327, 69.
27. Nędzarek, A.; Tórz, A.; Karakiewicz, B.; Clark, J.S.; Laszczyńska, M.; Kaleta, A.; Adler, G. Concentrations of heavy metals (Mn, Co, Ni, Cr, Ag, Pb) in coffee. *Acta Biochim. Polonica*, 2013, 60, 623–627.
28. Dos Santos, J.S.; Dos Santos, M.L.P.; Conti, M.M.; Dos Santos, S.N.; De Oliveira, E. Evaluation of some metals in Brazilian coffees cultivated during the process of conversion from conventional to organic agriculture. *Food Chem.* 2009, 115, 1405–1410.
29. Offsetdrukkerij Haveka B.V., Alblasserdam" COFFEE AND CARDIOVASCULAR RISK; AN EPIDEMIOLOGICAL STUDY. Oms lag Pieter-Jan Kersbergen 2004.
30. Wagesho, Y.; Chandravanshi, B.S. Levels of essential and non-essential metals in ginger (*Zingiber officinale*) cultivated in Ethiopia. *Springer Plus*, 2015, 4, Article No. 127. DOI: 10.1186/s40064-015-0899-5.
31. Ayele, E.; Urga, K.; Chandravanshi, B.S. Effect of cooking temperature on mineral content and antinutritional factors of yam and taro grown in southern Ethiopia. *Int. J. Food Eng.* 2015, 11, 371–382.
32. Weldegebriel, Y.; Chandravanshi, B.S.; Wondimu, T. Concentration levels of metals in vegetables grown in soils irrigated with river water in Addis Ababa, Ethiopia. *Ecotoxicol. Environ. Saf.* 2012, 77, 57–63.
33. 13. Illy, E. The complexity of coffee. *Sci. Am.* 2002, 286, 86–91.
34. Anderson, K.A.; Smith, B.W. Chemical profiling to differentiate geographic growing origins of coffee. *J. Agric. Food Chem.* 2002, 50, 2068–2075.
35. Suseela, B.; Bhalke, S.; Kumar, A.V.; Tripathi, R.M.; Sastry, V.N. Daily intake of trace metals through coffee consumption in India. *Food Addit. Contam.* 2001, 18, 115–120.
36. Gebretsadik, A.T.; Berhanu, T.; Kefarge, B. Levels of selected essential and nonessential metals in roasted coffee beans of Yirgacheffe and Sidama, Ethiopia. *Am. J. Environ. Protect.* 2015, 4, 188–192.

37. Ashu, R.; Chandravanshi, B.S. Concentration levels of metals in commercially available Ethiopian roasted coffee powders and their infusions. *Bull. Chem. Soc. Ethiop.* 2011, 25, 11–24.
38. Horžić D., Komes D., Belščak A., Kovačević Ganić K., Iveković D., Karlović D. (2009): The composition of polyphenols and methylxanthines in teas and herbal infusions. *Food Chemistry*, 115: 441–448. Rapić V. (1994):
39. Postupci priprave I, izolacije organskih spojeva, Školska knjiga, Zagreb. Re R., Pellegrini N., Proteggente A., et al.. Antioxidant activity applying an improved ABTS radical cation decolourisation assay. *Free Radical Biology & Medicine*, 2000, 26: 1231–1237.

Tables

Table 1 Physical and Chemical Properties of Coffee Samples(n=13)		
S.no	Parameter	Mean \pmSD
Physical Properties		
1	PH	4.68 \pm 0.57
2	Conductivity ms/cm	0.85 \pm 0.36
3	TDS mg/L	419.92 \pm 177.35
4	Temperature °C	19.58 \pm 0.09
5	Color CU	6856.54 \pm 2999.06
6	Turbidity NTU	32.20 \pm 27.09
7	Degree of color	Deep/Faint
Chemical Properties		
1	Sulfate SO ₄ mg/L	25 \pm 5.08
2	Sulfide mg/L	1.20 \pm 1.42
3	Phosphate PO ₄ mg/L	40.13 \pm 28.10
4	Ammonia NH ₄ mg/L	3.07 \pm 3.20
5	Nitrate NO ₃ mg/l	45.53 \pm 36.58
6	Nitrite NO ₂ mg/L	0.23 \pm 0.255

Table 2 Concentration of Non Toxic Metal Concentration in Coffee Samples(n=13)

Metals	Mean and SD	Range
Ca	24.873±6.76	6.76-32.09
Fe	6.670±4.88	0.82-14.35
K	235.985±100.05	21.31-427.84
Mg	407.024±226.56	43.18-767.62
Mn	8.637±10.14	0.48-28.69
Mo	0.0143±0.01	0-0.04
Na	333.865±247.35	6.84-564.74
Se	0.271±0.22	0-574
V	0.939±0.36	0.340-1.60

Table 3 Concentration of Toxic Metal Concentration in Coffee		
Metals	Mean and SD mg/kg	Range
Al	11.040±10.03	0.87-31.76
Cd	0.802 ±2.52	0-8.01
Cu	2.436±3.02	0.133-10
Ni	0.072±0.1100	0-0.258
Pb	7.571±9.266	0-23.88
Si	23.480±27.32	0.52-88.83
Sr	9.093±14.39	0-33.78
V	0.751±0.42	0.34-1.60
Zn	1.853±1.66	0.003-4.59

Figure (1) Average Level concentrations of phosphate, ammonia and nitrate between different coffee samples

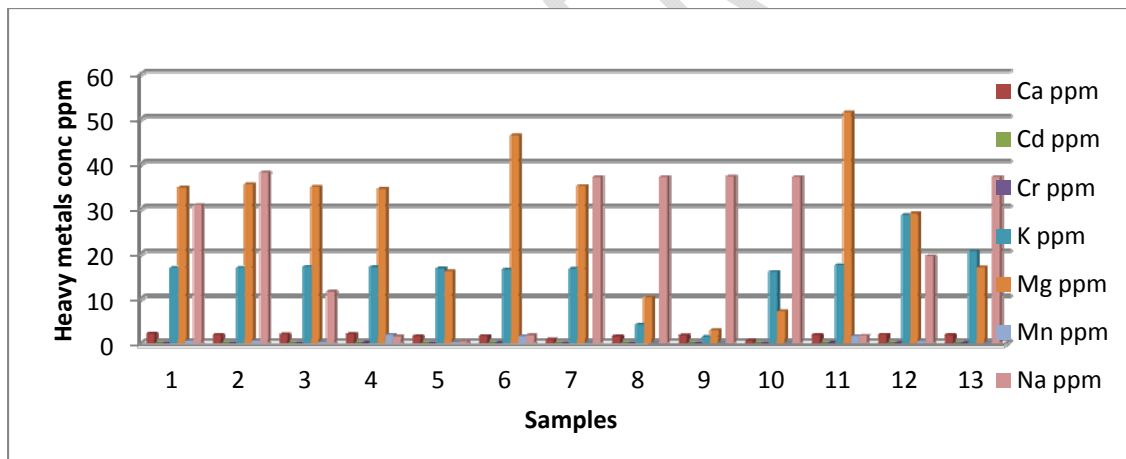
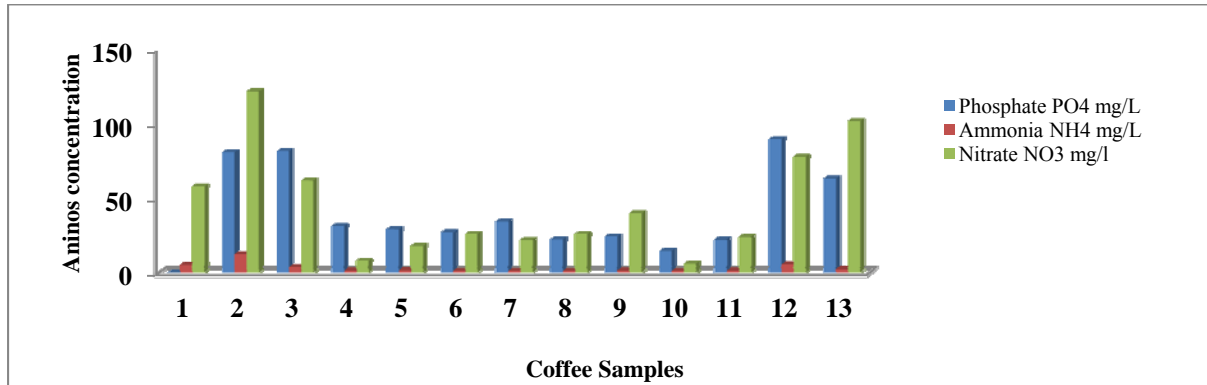


Figure 2 Non toxic heavy metals concentrations in different coffees samples

UNDER PEER REVIEW