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Essential and Non-Essential Metals in Soft Drinks Consumed and Sold In Port Harcourt, Nigeria

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***ABSTRACT:** Some essential (Iron Fe, Zinc Zn, Copper, Cu) and non-essential (Cadmium, Cd, and Nickel, Ni, Lead, Pb) metal concentrations were determined in canned and bottled samples of different soft drinks sold and consumed in Port Harcourt. The aim was to determine the levels of these metals in the common soft drinks generally consumed in Port Harcourt. Analysis was done by Flame Atomic Absorption Spectrophotometry. The mean concentrations of heavy metals were in the order Fe>Zn>Pb>Cu. The result showed Iron concentration ranged from 0.60 mg/l in LCSD to 3.67 mg/l in MGD, followed by AMD with a value of 3.215 mg/l. Iron mean concentration was 2.20±1.2 mg/l. The highest iron content was in MGD (3.67 mg/l) while the lowest was in LCSD drink (0.60 mg/l). Zinc ranged from 0.10 mg/l in CCD to 0.40 mg/l in MGD. The mean concentration was 0.194±0.12 mg/l. The levels of Copper, Cadmium, Lead, and Nickel found in all of the five (5) soft drink brands were below detectable levels (<0.001mg/l). Iron had the highest concentration of metals followed by Zinc and the two exceeded the WHO limits of 0.3 and 0.2 mg/l limits.*
***Keywords:** Essential and Non-Essential metals, soft drinks, Atomic Absorption, Port Harcourt.*

1.0 INTRODUCTION

Soft drink isalso called soda, pop, coke,soda pop, fizzy drink, tonic, seltzer, mineral, sparkling water or carbonated beverage and is more commonly referred to by regional names in many countries of the world (Vaux andGolder, *2003, Harvard Survey, 2003*). It is a beverage that typically contains water (often, but not alwayscarbonated water), usually a sweetener and a flavoring agent(Vaux andGolder, *2003*). Soft drinks, also known as ready-to-drink beverages are sweetened water-based non-alcoholic beverages, mostly with balanced acidity (Eyong*et al., 2010*, Ofori*et al.*, 2013, Adepoju-Bello, 2012).The sweetener may be sugar, high fructose corn syrup, fruit juice, sugar substitute(in the case of diet drinks) (Vaux andGolder, *2003*).The soft drinks are mostly carbonated usually prepared from a concentrated syrup containing sugar, flavouring essence, citric acid and a preservative, Sodium Benzoate (Ofori*et al*., 2013). Benzoic acid is commonly used as a preservative (Kirk, 1991). Soft drinks are the usual beverages used in most festivities and celebrations in Nigeria as well as elsewhere. These celebrations include marriages, weddings, naming of babies,funerals, etc.

The presence of metallic impurities in soft drinks can constitute health hazards to the public (Onianwa*et al.*, 1999; Bakare-Odunola, 2005; Krepcio*et al.*, 2005, Adepoju-Bello*et al.*, 2012). Soft drink contamination by heavy metalshas therefore become a matter of public health concern. Some essential metals are involved in numerous biochemical processes and adequate intake of them prevents deficiency diseases (Ofori *et al.*, 2013).Although some metals are essential for soft drink, the ranges between beneficial and toxic levels in those heavy metals are usually small. There is an increasing concern about the health effects on humans due to continuous consumption of soft drinks contaminated with heavy metals.Heavy metal composition of food is of interest because of their essential or toxic nature (Al-Mayaly, 2013). For example, iron, zinc, copper, chromium, cobalt, and manganese are essential, while lead, cadmium, nickel, and mercury are toxic at certain levels (Al-Mayaly, 2013, Onianwa*et al*., 1999).

Many studies have been conducted on metal levels in soft drinks (Maff, 1998; Onianwa*et al., 1999, 2001;* Ashraf *et al., 2000*, Krejpcio *et al., 2005 and* Maduabuchi *et al., 2006).* Krejpcio*et al.* (2005),reported Lead, Cadmium, Copper and Zinc levels as 0.020-0.46mg/l, 0.004-0.060mg/l, 0.047-1.840 mg/l, and 0.063-3.39 mg/l respectively in a total of 66 fruit juice samples examined in Poland. The occurrence of heavy metals in water and several foods has been investigated in Turkey (Bayham&Yentur, 1989 and Oktem*et al*., 2004). Maduabuchi*et al.* (2006), reported Cadmium levels as 0.003-0.081mg/l in canned drinks and 0.006-0.071 mg/l in non canned drinks.Onianwa*et al.* (1999), reported mean levels of 0.003-0.007 ppm Cd, 0.003-0.032 ppm Co, 0.001-0.030 ppm Cr, 0.001-1.02 ppm Cu, 0.56-6.36 ppm Ni, 0.030-0.070 ppm Pb and 0.020-1.10 ppm Zn in carbonated soft drinks (Bingol*et al.*, 2010).

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In another study, Lead, Arsenic, and Cadmium contents were determined as 0.02-0.05mg/kg, < 0.1mg/kg, and 0.0004-0.001mg/kg, respectively, in non-alcoholic beverage samples from a total of 100 samples (Maff, 1998).Lead and Cadmium toxicityis well documented and recognized as major environmental health risks throughout the world (Bingol*et al.*, 2010, Krejpcio*et al*., 2005 and Rubio *et al*., 2006). Lead affects humans and animals of all ages, however, the effects of Lead are most serious in young children (Adepoju-Bello, 2012). Cadmium is a toxic and carcinogenic element (Krejpcio*et al*., 2005 and Rubio *et al*., 2006).Cadmium intake in relatively high amounts can be detrimental to human health. Over a long period of intake, Cadmium may accumulate in the kidney and liver and because of its long biological half life, may lead to kidney damage (Maduabuchi*et al*., 2006).After acute and chronic exposures, it causes a variety of adverse health effects to humans such as dermal changes, respiratory, pulmonary, cardiovascular, gastrointestinal, hematological hepatic, renal, neurological, developmental reproductive, immunologic, genotoxic, mutagenic, and carcinogenic effects (Mandal& Suzuki, 2002).

Ashraf *et al*. (2000), reported Arsenic level as 0.837 mg/l in 34 soft drinks in Pakistan. Onianwa*et al*. (1999), reported Cadmium, Copper, Lead, and Zinc levels in carbonated soft drinks in Nigeria. Maduabuchi*et al*. (2006), reported cadmium levels in canned drinks and in non-canned drinks. Copper is one of the essential trace elements. The deficiency of this element is manifested by impaired haematopoesis, bone metabolism, disorders of the digestive, cardiovascular and nervous systems. Sporadically, copper nitroxicatrons are described. The acute exposure to Copper containing dust is manifested by metal fine fever (Krizek*et al*., 1997). Zinc deficiency, resulting from poor diet, alcoholism, and malabsorption, causes dwarfism, hypoqonadism, and dermatitis while the toxicity of Zinc due to excessive intake may lead to electrolyte imbalance, nausea, anaemia, and lethargy (Onionwa*et al*., 2001).

It is well known that an excess or deficiency of trace metals present in the human body can cause harmful effects (Zahir*et al.*, 2009). For example, an excess of Cu in the body causes Wilson's disease while a deficiency of Zn is responsible for retarded body growth (Olivaries*et al*., 1996).The objective of the present study was to determine essential and non-essential metal contents of Cd, Ni, Pb, Fe, Cu and Zn in some soda and malt drinks sold in Port Harcourt. Soft drinks are common preference among individuals. With the changing life style and income levels, people are now shifting their consumption patterns to soft drinks.

2.0 Materials and Methods

Materials

A total number of five samples, from five different brands, were investigated for some essential and heavy metal presence in soft drinks (carbonated drinks) in 2014. These soft drinks were bought from several stores in mile 3 market in Port Harcourt. Multi element standards (Iron, Copper, Zinc, Lead, Cadmium, Nickel) were purchased from high-purity standards. All reagents were of analytical grade. Flame Atomic Absorption Spectrophotometric (FAAS) methods were used for the quantitative analysis of these essential and heavy metals in all samples. To determine the heavy metal levels, Association of Official Analytical Chemists (AOAC) methods were used (AOAC, 1996, 2003 and Jorhem, 1993).

Methods

To determine the heavy metals levels, AOAC methods were used (AOAC 1986, 2003; Jorhem 1993). A 30ml soft drink sample was allowed to rest for 24hrs and for the evaporation of the gases. Subsequently, 5ml HNO_3 65% was added to 5 mlsof the sample. A hot plate was used for the digestion and dissolution of the experimentalsamples which were dissolved at 190^{o}C and 400 psi pressure in Mars 5 apparatus (vessel type XKP 1500, CEM, Matthews, USA). After further 20minute processing, the samples were made up with deionizer water. Then 1% HNO_3 solution was passed through the apparatus and it was then cleaned. The heavy metals were analyzed by Flame Atomic Absorption Spectrophotometry (FAAS). The calibration curves were constructed using a series of dilutions containing different concentrations of heavy metals. The readings were taken at the wavelength of Iron, Copper, Zinc, Lead, Cadmium and Nickel corresponding to 248.3nm, 324.7nm, 213.9nm, 217nm, 228nm and 232.0nm respectively.Air/Acetylene gas was used for all the analyses.

Study Area Description

The study area was Mile 3 market, situated in Southern part of Port Harcourt City Local Government Area, in Rivers State, Port Harcourt, Nigeria (Figure 1).

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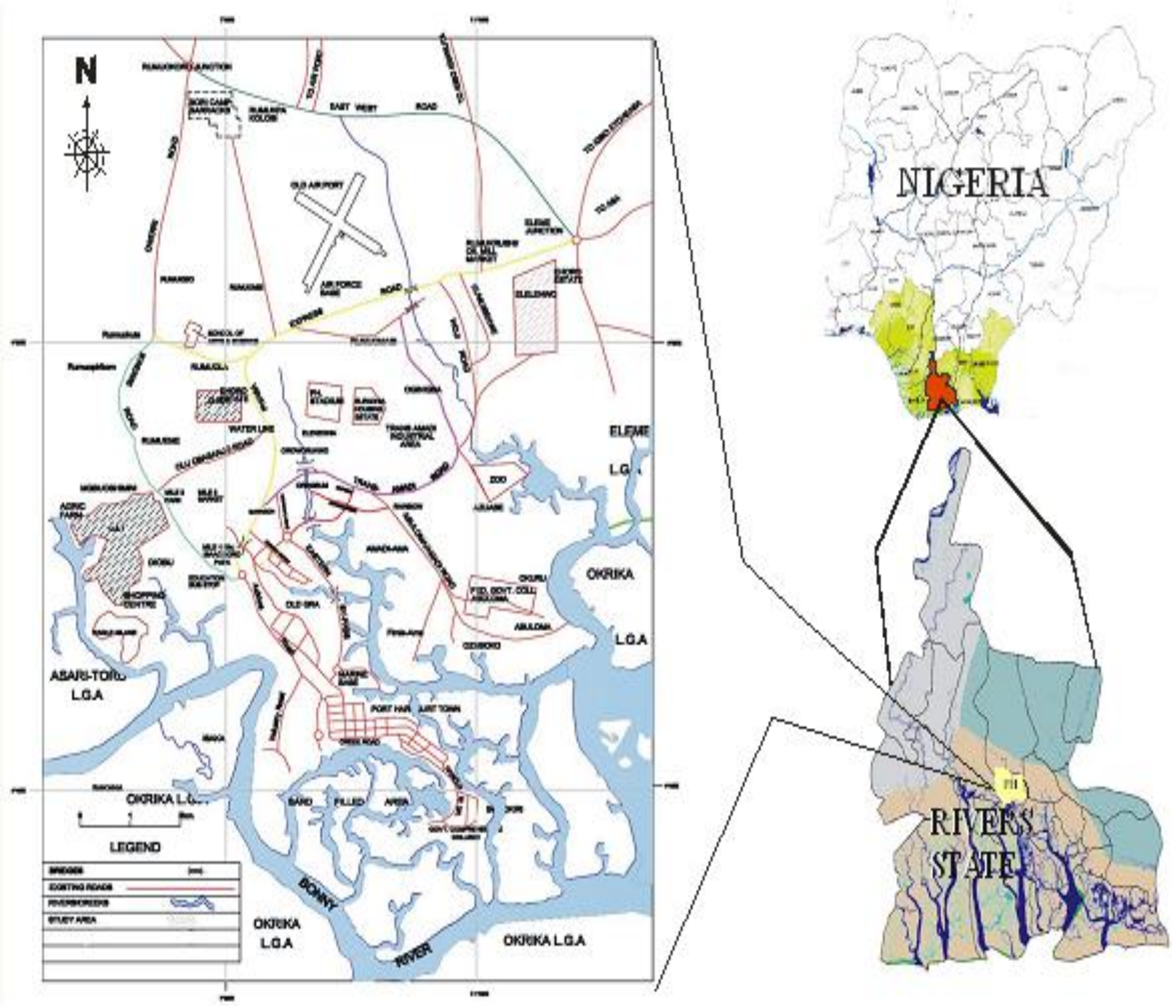

Fig. 1: Map of Port Harcourt showing the study area

3.0 Results and Discussion

Results

Iron concentration ranged from 0.60mg/l in LCSDsoft drink to 3.67mg/l in MGD, followed by AMD with a value of 3.215 mg/l (Fig. 2). Iron mean concentration was 2.20±1.2mg/l.The highest iron content was in MGD (3.67 mg/l) while the lowest was in LCSD drink (0.60 mg/l) (Fig. 2).Zinc ranged from 0.10 mg/l in CCD to 0.40 mg/l in MGD (Fig. 2). The meanconcentration was 0.194±0.12 mg/l. Copper, lead, Cadmium, Nickel concentrations were less than <0.001 mg/l in all the five (5) brands of drinks studied (Figs. 3, 4, 5& 6). The order of heavy metalconcentrations in terms of magnitude was Fe>Zn>Pb>Cu for soft drinks.

Metal Concentrations in all Brands Studied

Only two (2) metals, Fe and Zn were detected in all the brands studied (Fig. 5). Iron had the highest concentration of metals followed by Zinc. MGD brand of Malt had the highest concentration ofFe followed by AMD. LCSD had the least Iron concentration (Figs. 2&3). Cu, Pb, Cd and Ni were less than their detection limits (<0.001mg/l).

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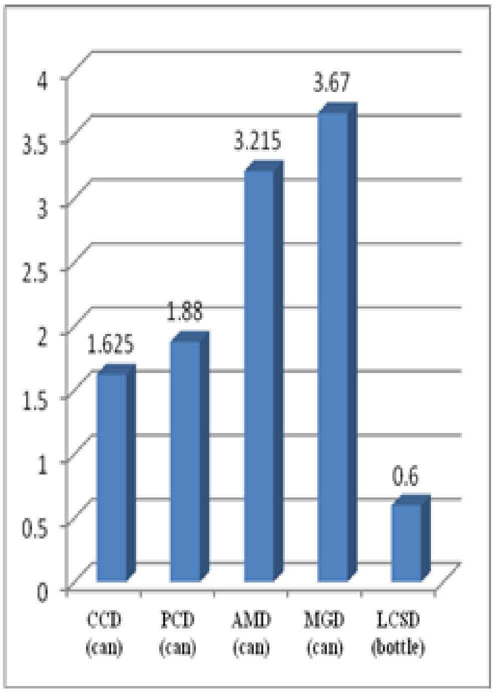

Fig. 2: Iron concentration in all brands of drinks studied.

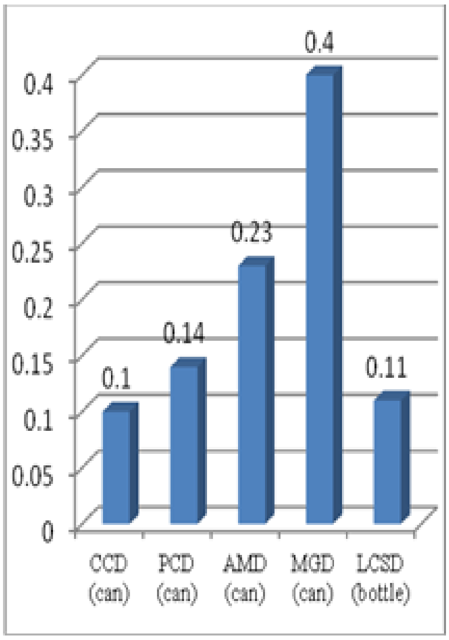

Fig. 3: Zinc concentrations in all brands of drinks studied.

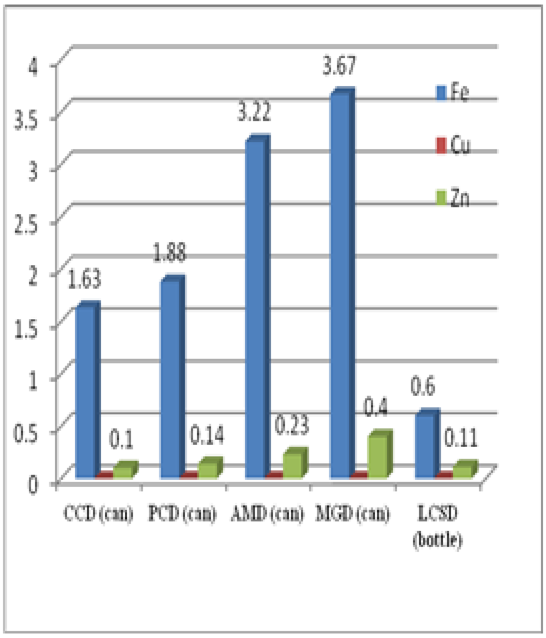

Fig. 4: Metal concentrations in all Brands of soft drinks studied

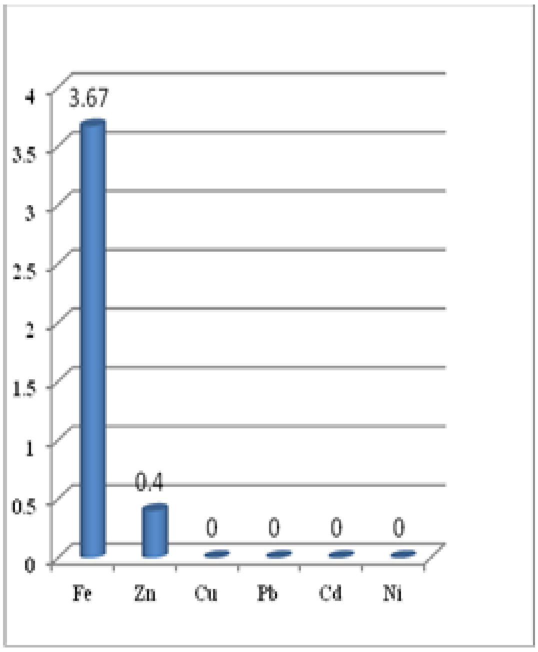

Fig. 5: Metal distribution in all Brands of soft drinks studied

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Table 1: Heavy metal concentrations in different brands of soft drinks (mg/l) in Port Harcourt

S/N	Sample Identity	Essential Metals			Heavy Metals		
		Fe (mg/l)	Cu (mg/l)	Zn (mg/l)	Pb (mg/l)	Cd (mg/l)	Ni (mg/l)
1.	CCD (can)	1.625	<0.001	0.100	<0.001	<0.001	<0.001
2.	PCD (can)	1.880	<0.001	0.140	<0.001	<0.001	<0.001
3.	AMD (can)	3.215	<0.001	0.225	<0.001	<0.001	<0.001
4.	MGD (can)	3.670	<0.001	0.395	<0.001	<0.001	<0.001
5.	LCSD (bottle)	0.600	<0.001	0.110	<0.001	<0.001	<0.001
	Mean	2.198	<0.001	0.194	<0.001	<0.001	<0.001
	WHO Standard	0.3	3.0	0.2	0.01	0.005	0.10

DISCUSSION

Iron was above the WHO Standard of 0.3 mg/l (Figs. 2&3).WHO has recommended a safe limit of 0.3 mg/l for iron in drinking water and 10-50 mg per day of iron as daily requirement for humans depending on age, sex, physiological status and iron bioavailability (FAO/UN, 1998).In this study, the maximum Iron concentration determined was 3.670 (0.60-3.670)mg/l which was above the WHO safe limit of 0.3 mg/l (WHO, 2006),but this concentration fall within the 10-50 mg per day as iron requirement for human body depending on age, sex, and iron bioavailability. Oforiet *al*. (2013),had reported Iron concentration ranging from 5.68-13.41mg/l in their study of soft drinks in Ghana and our findings in Port Harcourt are much less than reported.High Iron content has been attributed to leaching from the container into the drinks. Iron (Fe) is an essential metal and deficiency (anemia) for instance, affects one third of the worldpopulation (Ofori*et al.*,2013). Some essential metals are involved in numerous biochemical processes and adequate intake of certain essential metals relates to the prevention of deficiency diseases. On the other hand, excessive iron intake has been associated with an overall increase risk of colorectal cancer (Senesse*et at*., 2004). Metals such as copper (Cu), zinc (Zn) or iron (Fe) are essential for important biochemical and physiological functions and necessary for maintaining good health throughout life (Nabrzyski, 2007). They combine with certain proteins to produce enzymes that act as catalysts to help in a number of body functions (Grembecka and Szefer, 2011).

Zincrange of 0.10-0.395 mg/l obtained in this study, is higher than WHO safe limit of 0.20 mg/l.Ofori*et al.*(2013),reported a range of 0.42-2.06 (1.07±0.66) mg/l for Zinc in their study of soft drinks in Ghana. Our finding is lower than that reported by Ofori*et al.*(2013) and the WHO standard of 0.2 mg/l.Adepoju-Bello *et al.* (2012), reported no detectable levels for Zinc in soft drinks in Lagos. Madubuchi*et al*. (2006) and Krejpcio*et al*. (2005), reported Zinc levels of 0.063-3.39 mg/l for Zinc in their study. The Zinc level reported is higher than that observed in our study. Onianwa *et al*. (2001), reported Zinc level of 0.15±0.03 ppm in carbonated soft drinks in Nigeria; this corroborates our findings. Bingol *et al.* (2010), reportedzinc level of 0.009-0.90 (0.143±0.012) ppm, Znconstitutes 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 (Adepoju-Bello *et al.*, 2012). Zinc deficiency, resulting from poor diet, alcoholism and malabsorption, causes dwarfism, hypognadism and dermatitis, while toxicity of Zn due to excessive intake may lead to electrolyte imbalance, nausea, anemia and lethargy (Onionwa, *et al*., 2001, Ma and Betts, 2000). Zinc is an essential mineral that is found in almost every cell and its toxicity has been seen in both acute and chronic forms (Adepoju-Bello *et al.*, 2012). Intakes of 150 to 450 mg of zinc per day has been associated with low copper status, altered iron function, reduced immune function, and reduced levels of high-density lipoproteins (the good cholesterol). One case report cited severe nausea and vomiting within 30 min after the person ingested four

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grams of zinc gluconate (570 mg elemental zinc) (Valko*et al.,* 2005).

Copperwas not detected (<0.001) mg/l in this study and was below WHO limit of 3.0 mg/l. Ofori*et al*. (2013), reported Copper level in the range of 0.33- 0.77 (0.34±0.05) mg/l in their study of soft drinks.This is higher than our Cu level of not detectable value. Bingol *et al.* (2010), reported copper levels of 0.004 -0.770 (0.070±0.009) mg/l in soft drinks in Turkey.Copper and zinc are essential trace metals according to Ma *and Betts* (2000), and the concentration of copper in this study is within the safe limit set by WHO i.e. 3.0 mg/l(WHO, 2006). The copper levels in soft drink samples in this study, do not pose any threat to public health. Madubuchi *et al*. (2006), and Krejpcio *et al*. (2005), reported Copper levels ranging from 0.047-1.840 mg/l. Bingol *et al. (*2010), reported Copper levels of 0.004 -0.770 (0.070±0.009) ppm in soft drinks.These are all higher than the findings of our study.Theadult human body contains about 1.5-2.0 ppm of Cu which is essential as a constituent of some metallo-enzymes and is required in haemoglobin synthesis and in the catalysis of metabolic oxidation. Symptoms of Cu deficiency in humans include bone demineralization, depressed growth, depigmentation and gastro-intestinal disturbances, among others, while toxicity due to excessive intake has been reported to cause liver cirrhosis, dermatitis and neurological disorders (Silvestre, *et al.*, 2000).

Leadconcentration was not detectable (<0.001) mg/l in this study and was below WHO limit of 0.01 mg/l. Madubuchi*et al*. (2006) and Krejpcio *et al*. (2005), reported Lead levels ranging from 0.020-0.46 mg/l,which exceed WHO limit of 0.01 mg/l.Adepoju-Bello (2012), reported lead levels in soft drinks ranging from not detectable -0.0002 mg/l, in Lagos, which is below the WHO limit of 0.01 mg/l. Other researchers have reported lead levels in soft drinks reaching 2.78 mg/l which is far above the safe limit of 0.01 mg/l recommended by WHO (Ofori, 2013); Bingol*et al.* (2010), reported lead level of 0.004-0.091 (0.029±0.002) ppm. According to Venugopal and Luckey (1975), lead toxicity is associated with abnormal size and haemoglobin content of the erythrocytes, hyper-stimulation of erythropoiesis and inhibition of haeme synthesis. Lead and cadmium are two potentially harmful metals that have aroused considerable concern (Cabrera, 1995). Lead and cadmium toxicity is well documented and is recognized as a major environmental health risk throughout the globe (Bingol*et al.,* 2010,). Lead is known to affect humans and animals of all ages; however, the effects of lead are most serious in young children (Adepoju-Bello, 2012).Because of their high toxicity, Arsenic, Lead and Cadmium need to be quantified in food and beverages (Barbaste*et al.,* 2003).

Cadmium concentration was not detectable (<0.001) mg/l in this study and was below WHO limit of 0.005 mg/l. Maduabuchi *et al*. (2006), reported Cadmium levels ranging from 0.003-0.081 mg/l in canned drinks, which is higher than those obtained in this study. In addition, Onianwa*et al*. (2001), reported Cadmium levels as 0.002±0.005 ppm, in carbonated soft drinks in Nigeria. Bingol *et al. (*2010), reported cadmium level of 0.0001-0.011(0.005±0.0003) ppm in soft drinks in Turkey.Cadmium is a toxic and carcinogenic element (Rubio *et al.*, 2006). Cadmium intake in relatively high amounts can be detrimental to human health. Over a long period of intake, Cadmium may accumulate in the kidney and liver because of its long biological half life and may lead to kidney damage (Maduabuchi *et al.*, 2006).

Nickel concentration was not detectable (<0.001) mg/l in this study and was below WHO limit of 0.10 mg/l.Levels ranging from 0.016 to 0.063 mg/l were reported by Adepoju-Bello (2012) in soft drinks in Lagos.Foodstuffs naturally contain small amounts of nickel (Adepoju-Bello, 2012). Chocolate and fats are known to contain severely high quantities (Wilson, 2009). Toxicity of nickel has been reported to include: higher chances of development of lung cancer, nose cancer, larynx cancer and prostate cancer, sickness and dizziness after exposure to nickel gas, lung embolism, respiratory failure, birth defects, asthma, chronic bronchitis and allergic reactions (Kasprzak et al., 2003). The presence of metallic impurities in soft drinks can constitute health hazards to the public (Onianwa *et al.*, 1999; Bakare-Odunola, 2005; Krepcio *et al.*, 2005). Heavy metals composition of foods is of interest because of their essential or toxic nature. For example, iron, zinc, copper, chromium, cobalt, and manganese are essential, while lead, cadmium, nickel, and mercury are toxic at certain levels (Onianwa *et al.* 1999).

Recommendations

Further investigations are recommended into the level of many metals in moresoft drinks and vegetables sold and consumed in Port Harcourt to document and establish human exposure to heavy metals.

CONCLUSION

The study showed high Iron and Zinc contents that exceeded WHO 0.3 mg/l and 0.2 mg/l limitsfor Iron and Zinc in

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drinks respectively. Iron (Fe) and Zinc (Zn) were the only metals detected in five brands of soft drinks studied.Humans taking canned malt drinks should be aware of high Iron and zinc contents that exceed recommendedWHO levels. For this reason, soft drinks producers may want to take steps in all processes to monitorand prevent contamination by heavy metals.

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