Int. J. Hum. Capital Urban Manage., 2(2): 89-100, Spring 2017
DOI: 10.22034/ijhcum.2017.02.02.001

ORIGINAL RESEARCH PAPER

Frequency of electronics waste generated heavy metals in urban waterways

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Received 20 November 2016; revised 28 January 2017; accepted 23 March 2017; available online 1 April 2017

ABSTRACT: Heavy metals are one of the dreadful environmental pollutants. Its toxicity is a menace to the ecosystem and has attracted global concern over the decades. The attendant uncontrolled disposal and recycling of electronic-waste (e-waste) has greatly influence the elevated concentration of heavy metals observed in Nigeria waterways. This study was carried out to investigate the frequency of the deadly heavy metals as part of public health intervention. The study was a cross sectional design in which waterways from the three geographical zones of Kwara State, Nigeria were sampled by integrated composite method and analyzed for physical and chemical parameters during the dry and rainy season. High frequency of e-waste generated heavy metals in the urban waterways was observed with respect to influence of settlement, geographical zones and seasonal variation in the study area. The mean concentrations of the heavy metals analyzed showed a decreasing trend in their quantity as Cr >Cd>Pb>Hg in both seasons. Statistically, no significant difference in densities of Lead, Mercury and Chromium with respect to season (P_{cal} = 0.482 in chromium, P_{cal} = 0.067 in Lead, P_{cal} = 0.146 in Mercury, P > 0.05). However, there was significant difference in frequency of Cadmium by season (P_{cal} = 0.001, P < 0.05). Assessment of the findings with respect to geographical zone revealed a significant difference in the mean distribution of Chromium during both seasons. Heavy metals were also recorded to be higher in the urban areas than the rural areas.

KEYWORDS: *Electronic-waste; Heavy metals; Kwara State toxicity; Waterways*

INTRODUCTION

Water pollution therefore poses a serious threat to the well-being of the ecosystem (Halder and Islam, 2015). Abdullah (2013) documented that the principal source of pollutants in drinking water is heavy metals. The contamination of waterways by heavy metals has attracted global attention as a result of its persistence and toxicity (Onwughara *et al.,* 2011; Ahmed *et al.,* 2015a; 2015b; Islam *et al.,* 2015; Ali *et al.,* 2016). Heavy metals are environmental pollutants and their toxicity is a problem of increasing concern (Nagajyoti *et al.,* 2010; Jaishankar *et al.,* 2014). Though the levels of heavy metals contamination of the environment have declined in recent decades in the developed countries, the developing countries heavy metal pollution is on the increase (Neal and Guilarte, 2012). Elevated levels of heavy metals contamination was reported in Asian and African countries, particularly in their urban environments (Gong *et al.,* 2010; Yu *et al.,* 2012; Huang

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et al., 2014). It was reported that a major source of heavy metals contamination in developing countries is from poor disposal and recycling of electronic waste (Grossman, 2006; Azuka, 2009; Onwughara *et al.,* 2011; Neal and Guilarte, 2012; Diaz-Barriga, 2013; Grant *et al.,* 2013). Electronic waste (e-waste) is any out of order piece of electrical and electronic equipment which has reached the end of its useful life and have been discarded by its owner as waste without the intent of re-use (Step initiative, 2014; Baldé *et al.,* 2015). It covers a broad and growing scope of electronic and electrical devices ranging from large household appliances such as refrigerators, air conditioners to personal computers and cellular phones (UNEP, 2007; Azuka, 2009). They are incorporated with heavy metals which have the ability to contaminate domestic waters and food chains (UNEP, 2007; Orisakwe and Frazolli, 2010; Frazolli *et al.,* 2010; Onwughara *et al.,* 2010a; Grant *et al.,* 2013). Onwughara *et al*. (2010b) reported that e-waste is often disposed with municipal solid waste into open dumps and directly into surface water use for domestic purposes in Nigeria. Leaching of toxic heavy metals can easily ensue via these routes of disposal which can contaminate surface and ground water eventually (Onwughara *et al.,* 2011).

Onwaghara et al. (2010a) and Osibanjo (2011) reported that Nigeria has the largest market for "second-hand" (*Tokunboh*) electronics device in Africa. This can be attributed to the present economic reality in Nigeria where majority of the populace are low-income earners and rely on *Tokunboh* to enable them bridge the digital divide considering that branded new electronic goods are relatively expensive for ordinary people (Puckett *et al.* 2005; Schmidt, 2006). Informal e-waste recycling involves dismantling of electronic and electrical equipments through primitive techniques in order to retrieve the valuable metals with little or no regards for worker's safety and environmental protection (Cobbing, 2008; Ladou and Lovgrove, 2008; Robinson, 2009; Shamim *et al.,* 2015). Nigeria was reported to host high-volume and cheap informal recycling of these valuable metals (Grant *et al.,* 2013). These techniques facilitate the release of toxic heavy metals in to the environment through handling and processing as many e-waste fractions cannot be managed appositely (Sepúlveda *et al.,* 2010; Konya *et al.,* 2015). All these enhance the possibilities of the waterways being exposed to e-waste-generated heavy metals thus, exposing the populace to toxic contamination through physical contact with soil and dust, and ingestion of contaminated locally produced comestible and drinking water (Wong *et al.,* 2007a; 2007b; Tsydenova and Bengtsson, 2011). Despite the dearth of scientific valid research findings, the public health effects of chemical exposure from the disposal and recycling of e-waste has been on the increase (Shamim *et al.,* 2015). The usual hazardous, toxic and non biodegradable e-waste generated heavy metals include cadmium, lead, mercury, arsenic, nickel, chromium, copper, manganese, zinc, iron and aluminium (Li *et al.,* 2011; Wath *et al.,* 2011; Shamim *et al.,* 2015). Many of these pollutants combine synergistically resulting in severe or different impacts than the cumulative effects of a single pollutant (UNEP, 2010). This study was carried out to investigate the frequency of some deadly heavy metals with respect to influence of settlements, geographical zone and seasonal variation in the three geographical zones across Kwara State, Nigeria in 2016.

MATERIALS AND METHODS

Study Area

Kwara State located in the north central geographical zone of Nigeria, was created in 1967 as one of the 12 federating units of the country. It shares boundary in the north with Niger State, in the south with Oyo, Osun and Ekiti States and in the East with Kogi State (Fig. 1). It has an international boundary in the west with the Republic of Benin (Fig. 1). It is situated between latitudes 11^0 2' and 11^0 45'N, longitude 2^0 45' and 6^0 4'E. Its location can be considered as midway between the Northern and Southern parts of Nigeria. It has two seasonal pattern; the dry and rain seasons. Monthly rainfall varies between 50.8mm and 241.3mm levels with the annual mean rainfall between 745.5mm and 1,409.2mm. Average atmosphere temperature is between 18^0C and 35^0C. Kwara state has 24 forest reserves covering 5,087.2sq km. The State has an estimated population of 2,371,000 (2009 projection), with an annual growth rate of 3.4%. The State has Sixteen Local Government Areas, grouped into 3 senatorial districts with Ilorin as the state capital. The different senatorial districts are what we considered as geographical zones in this study.

For the purpose of this research, river Moshi, river Moshe and river Tese were sampled from the Kwara north, while river Agba, river Atireke, river Alalubosa,

river Aluko, river Osere and river Asa were sampled from the central part of the study area. However, River Moro, River Awonga, River Basaa, River Osin, River Sosee and River Oyun were sampled from the southern zone (Fig. 2). Sampling was done in two season; dry season (between January and March, 2016) and rainy season (between July and September, 2016).

Study design and Collection of surface water

The study design was a cross sectional surveillance. Surface water samples were collected by integrated composite method. This was achieved by sampling from ten different points along each sampled river course and water pooled together. The procedure was repeated in triplicates for each sampled river into different pre-rinsed 2-litre glass containers. The analysis of physical parameters was done on site to ensure accurate measurement as obtained in the waterways.

Preservation of water

Samples for heavy metal analysis were treated immediately on-site with 2 millilitres (mL) of concentrated nitric acid prior to storage in cold. This ensures static metals oxidation states in cold condition and averts metals adsorption on storage container before laboratory analysis.

Laboratory testing

Analysis of the physical parameters

The physical parameters were analyzed by instrumentation method as described by Halder and

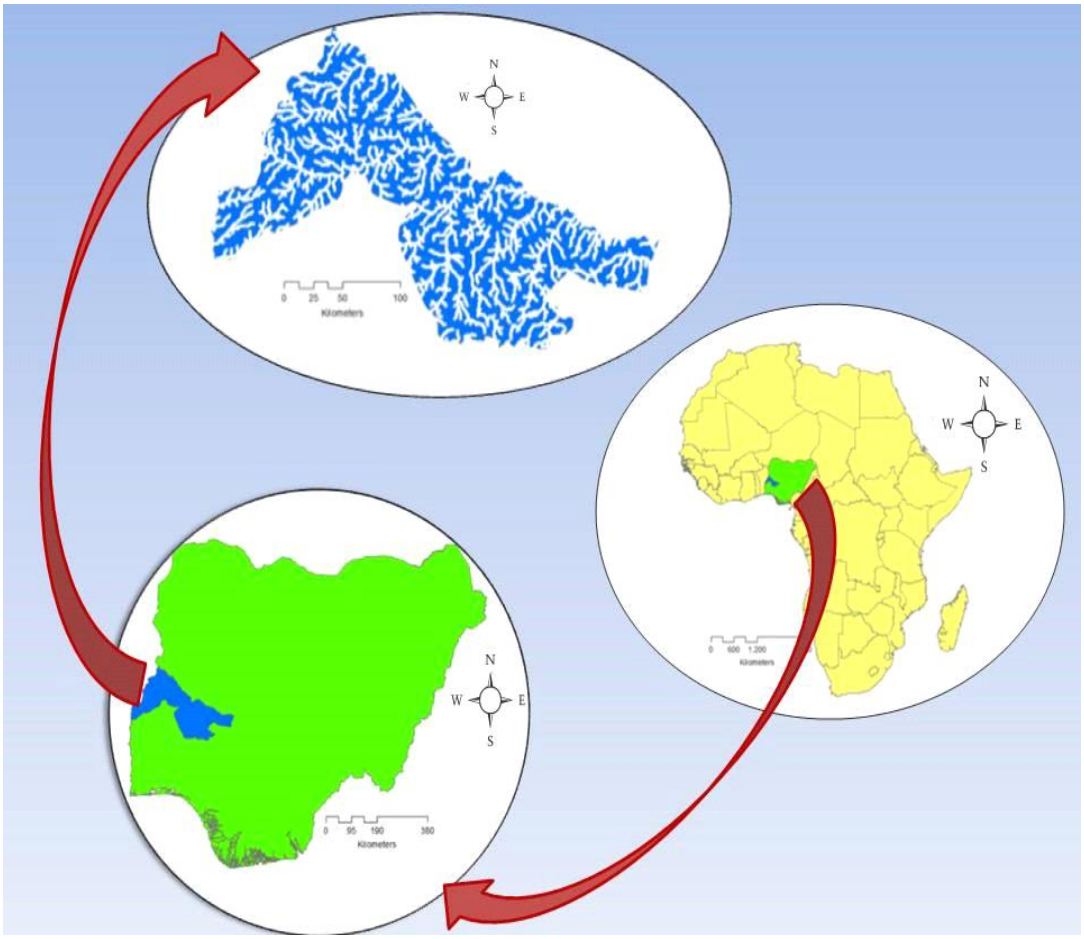

Fig. 1: Situation of the study area: Map of Africa (*insert* Nigeria), Nigeria (*insert* Kwara State) and drainage in Kwara State.

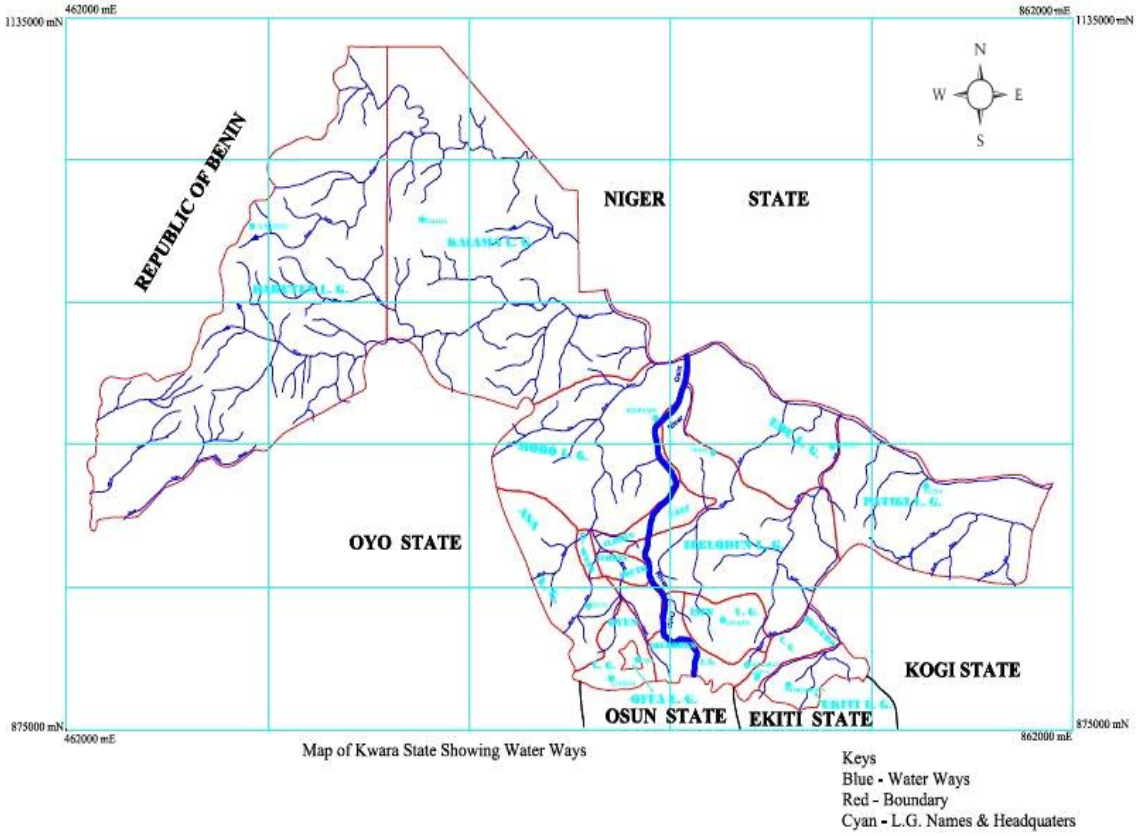

Fig. 2: Map of Kwara State showing waterways (KWGIS, 2016)

Islam, (2015). The physical parameters analyzed were, pH using pH meter, Temperature using thermometer, Turbidity using turbidimeter, Total dissolved solid (TDS) using microprocessor TDS meter and Electrical conductivity using microprocessor conductivity meter. All instruments were standardized prior to analysis, test was repeated and readings were taken in duplicates with only concordant values considered in the study.

Analysis of the chemical parameters

The heavy metals were analyzed using Bucks scientific atomic absorption spectrophometer (AAS) as described by Adeyemi *et al.* (2007). The heavy metals analyzed were, Lead (Pb), Mercury (Hg), Cadmium (Cd) and Chromium (Cr).

The analysis of chemical parameters was carried out at the Agronomy Department, University of Ibadan, Ibadan, Oyo State and Water Laboratory in Production Programming and Quality Control (PPQC) Department, Kaduna Refining and Petrochemical Company (Subsidiary of NNPC), Kaduna State where a bench space was procured for the research.

Each sample was digested before using Buck scientific atomic absorption spectrophotometer to determine the quantity of heavy metals from the sampled water. Preliminary digestion was carried out for each sample to ensure reliable quantification of the heavy metals.

Digestion of the samples

Fifteen (15) milliliter (mL) of each sample was digested with 10 mL of acid digestion mixture (Nitrc acid: Perchloric acid) in ratio 2:1. The samples were digested on Tecator digestion block for 2.5 h at a temperature of 250^{0}C. It was removed from the digestion block, allowed to cool and made up to 25 mL in 250 mL volume flask with double distilled demineralised water.

Statistical analysis

Statistical analysis was performed using GraphPad Prism statistical package soft version 6. All data were expressed as mean ± standard error of mean (S.E.M). Test of significance for the mean variation in frequency of heavy metals by zone, season and settlement was assessed by two-way ANOVA, followed by Uncorrected Fisher's LSD test for multiple comparisons. Data were analysis at 95% confidence interval and P-value less than 0.05 (PÂ0.05) was considered statistically significant.

RESULTS AND DISCUSSION

We initially proposed sampling equal number of rivers from the three geographical zones to avoid bias in our result and for proper interpretation of results. However, it was observed that most of the rivers from Northern zone dried up during the dry season, suggesting many of them were not major rivers but mere river tributaries. For this reason, we sampled three rivers from Northern zone and six rivers each from Central zone and Southern zone. The sample sites in the northern and southern zones were concentrated in rural settlements while the sites in central zone were within the urban settlements. Eight rivers were sampled from the rural settlement while seven were sampled from the urban settlement.

Distribution of some physical parameters in the study area

Distribution of the mean values of physical parameters analyzed in this study area during the dry and rainy season are as presented in Tables 1 and 2 respectively. These findings depict slight variation in surface temperature with maximum temperature of 30^0C during the dry season. This is not surprising because of the regular high temperature in this region. The mean pH values recorded for all the rivers sampled in this study was slightly alkaline. This is in agreement with Aktar *et al.* (2010) and Ogunkunle *et al.* (2016) which

Table 1: Mean distribution of some physical parameters in the study area during the dry season

Zones	Rivers	pH	Temperature (^{0}C)	Turbidity (NTU)	TDS (mg/L)	Electrical conductivity (µS/cm)
NZ	Moshin	8.40 ± 0.50	30 ± 0.6	2.03 ± 0.50	107.50 ± 1.5	179.20 ± 0.03
NZ	Moshe	8.80 ± 0.30	28 ± 0.7	2.05 ± 0.60	79.50 ± 0.5	132.55 ± 1.70
NZ	Tese	7.90 ± 0.50	27 ± 0.5	2.22 ± 0.40	78.00 ± 0.5	130.02 ± 0.02
CZ	Agba	7.80 ± 0.40	26 ± 0.2	1.83 ± 0.05	64.30 ± 0.3	106.66 ± 0.05
CZ	Atireke	7.70 ± 0.60	26 ± 0.5	1.90 ± 0.30	104.50 ± 0.4	174.65 ± 1.25
CZ	Alalubosa	7.60 ± 0.50	26 ± 0.2	1.95 ± 0.70	198.00 ± 0.6	230.08 ± 0.04
CZ	Aluko	7.90 ± 0.20	28 ± 0.4	2.03 ± 0.50	117.00 ± 0.2	125.05 ± 5.00
CZ	Osere	7.90 ± 0.30	28 ± 0.5	2.40 ± 0.60	146.00 ± 0.5	243.04 ± 15.00
CZ	Asa	8.20 ± 0.20	27 ± 0.6	1.81 ± 0.50	50.00 ± 0.5	84.40 ± 1.50
SZ	Moro	7.50 ± 0.50	27 ± 0.6	2.00 ± 0.60	76.00 ± 0.3	98.75 ± 0.05
SZ	Awonga	7.40 ± 0.10	26 ± 0.5	2.22 ± 0.50	90.00 ± 0.2	116.75 ± 0.33
SZ	Basaa	7.80 ± 0.50	26 ± 0.3	2.25 ± 0.60	95.50 ± 1.5	129.25 ± 0.33
SZ	Osin	7.20 ± 0.70	28 ± 0.2	2.01 ± 0.60	93.00 ± 1.0	154.67 ± 0.88
SZ	Sosee	7.50 ± 0.30	26 ± 0.4	1.99 ± 0.40	91.50 ± 0.7	152.20 ± 1.45
SZ	Oyun	6.80 ± 0.50	26 ± 0.2	2.30 ± 0.05	104.50 ± 0.3	178.33 ± 1.20
	NIS Standard	6.5-8.5	Ambient	5	500	1000
	WHO Standard	6.5-8.5	Ambient	5	600	1000

Table 2: Mean distribution of some physical parameters in the study area during the rainy season

Zones	Rivers	pH	Temperature (^{0}C)	Turbidity (NTU)	TDS (mg/L)	Electrical conductivity (µS/cm)
NZ	Moshin	8.2 ± 0.10	27 ± 1.7	2.20 ± 0.11	100.50 ± 3.2	139.40 ± 11.20
NZ	Moshe	7.8 ± 0.50	27 ± 1.2	1.90 ± 0.23	59.00 ± 2.3	121.55 ± 0.58
NZ	Tese	7.9 ± 0.20	27 ± 0.6	2.40 ± 0.12	48.00 ± 1.7	110.02 ± 4.63
CZ	Agba	7.8 ± 0.30	26 ± 1.2	2.20 ± 1.70	54.00 ± 1.2	100.06 ± 2.92
CZ	Atireke	8.2 ± 0.10	26 ± 0.6	2.50 ± 0.29	94.50 ± 0.9	74.65 ± 2.30
CZ	Alalubosa	8.0 ± 0.30	26 ± 0.6	2.00 ± 0.23	98.00 ± 0.6	130.08 ± 8.19
CZ	Aluko	7.3 ± 0.20	27 ± 1.2	2.80 ± 0.46	88.00 ± 4.6	111.05 ± 6.35
CZ	Osere	8.1 ± 0.10	26 ± 0.4	2.60 ± 1.70	90.00 ± 3.5	143.05 ± 7.51
CZ	Asa	8.2 ± 0.10	26 ± 0.6	2.00 ± 0.06	60.00 ± 2.9	90.40 ± 3.2
SZ	Moro	7.7 ± 0.40	26 ± 0.6	2.20 ± 0.12	66.00 ± 3.5	108.75 ± 4.62
SZ	Awonga	7.7 ± 0.30	26 ± 1.2	2.50 ± 0.12	95.00 ± 0.3	110.75 ± 1.15
SZ	Basaa	8.0 ± 0.50	28 ± 1.7	2.50 ± 0.06	95.50 ± 0.9	119.25 ± 5.20
SZ	Osin	7.9 ± 0.50	28 ± 1.2	2.00 ± 0.12	83.00 ± 1.7	135.15 ± 3.5
SZ	Sosee	8.2 ± 0.20	26 ± 0.4	2.50 ± 0.23	71.50 ± 2.3	142.20 ± 1.7
SZ	Oyun	8.1 ± 0.40	26 ± 1.7	2.80 ± 0.29	100.50 ± 3.2	159.20 ± 0.6
	NIS Standard	6.5-8.5	Ambient	5	500	1000
	WHO Standard	6.5-8.5	Ambient	5	600	1000

reported that alkalinity may probably be an indicator of decreased metals toxicity in water. Our findings also showed that the range mean values of turbidity, total dissolved solids and electrical conductivity in the sampled rivers were (1.75 – 2.90), (42.04 – 200.00) and (85.00 – 250.00) respectively; all falling within the permissible limit of (5 NTU, 500 mg/L and 1000 µS/cm) stated by NIS (2007) and (5 NTU, 600 mg/L and 1000 µS/cm) by WHO (2011).

Distribution of some chemical parameters in the study area

The heavy metals analyzed in this study were limited to those that can cause neurotoxicity: Chromium, Cadmium, Lead and Mercury as reported by Chen *et al*. (2011). The mean concentrations of the heavy metals analyzed showed a decreasing trend in their quantity as Cr Ã Cd Ã Pb Ã Hg in both seasons (Figs. 3 and 4).

Analysis by season

Mean chromium concentration within the waterways showed that river Alalubosa and river Atireke from central zone had the highest concentrations (0.268 ± 0.06 and 0.221 ± 0.03) and (0.318 ± 0.04 and 0.271 ± 0.03) for dry and rainy season respectively. The study also observed that there was no significance difference in the mean concentration of chromium by season when analyzed statistically ($P_{cal} = 0.482$, $P > 0.05$ (Fig. 5)).

Mean Cadmium concentration within the waterways showed that river Alalubosa from central zone had the highest concentrations (0.040 ± 0.01) and (0.045 ± 0.01) for the dry and rainy season respectively. Statistically, there was a significance difference in the mean density of cadmium by season ($P_{cal} = 0.001$, $P < 0.05$) (Fig. 5). This result is slightly lower than the result obtained by Ogunkunle *et al*. (2016), which could probably be due to difference in sources of water samples; while rivers

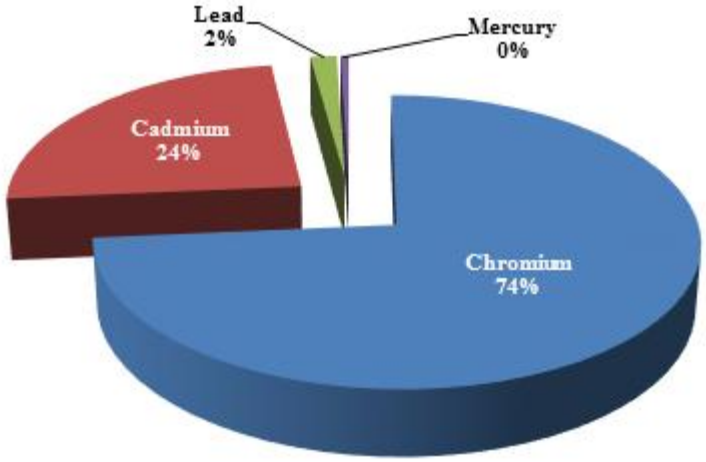

Fig. 3: Proportion of variation of heavy metals in the dry season, Cr >Cd > Pb> Hg

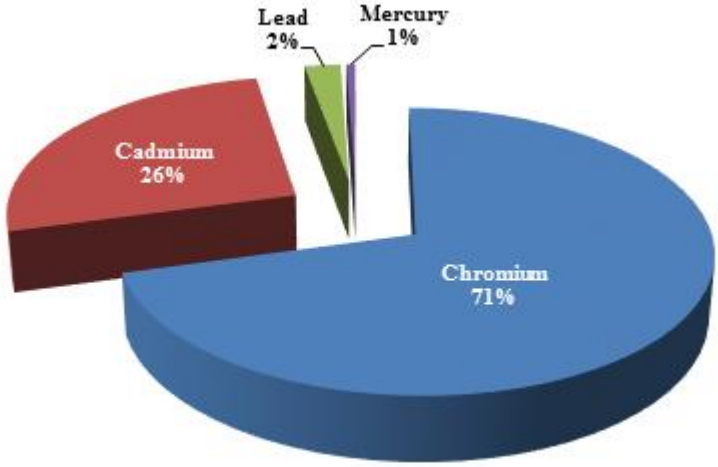

Fig. 4: Proportion of variation of heavy metals in the study area during the rainy season, Cr >Cd > Pb > Hg

were employed in this present study, dams were used in the previous work.

The mean concentrations of Chromium and Cadmium within the waterways as observed in the sampled area exceeded the maximum permissible standards (0.05mg/L for Chromium and 0.003mg/L for Cadmium) specified by (NIS, 2007) and (WHO, 2011) for drinking water respectively. This calls for immediate intervention as it can constitute toxicological menace on human and ecosystem. The sampled rivers are often used for domestic purposes supply by the rural commuters.

However, the mean concentrations of Lead and Mercury were observed to be within the permissible standards (0.01mg/L and 0.01mg/L for Lead and 0.001mg/L and 0.006mg/L for Mercury) specified by (NIS, 2007) and (WHO, 2011) for drinking water respectively. Statistically, variation in concentration of both metals

showed no significant difference in relation to season (P_{cal} = 0.067 in Lead, P_{cal} = 0.146 in Mercury, P > 0.05 (Fig. 5)). These levels of e-waste-generated heavy metals bio-accumulate through the food chain, animal tissue and excreted in edible products of animal origin not withstanding their quantity and eventually become biomagnified (Kierkegaard *et al.,* 2007; Frazolli *et al.,* 2010).

Analysis by zone in season

There was a significant difference in mean density of Chromium when compare to concentration of other heavy metals according to geographical zone during the dry season and rainy season (Figs. 6 and 7). The concentration of Chromium was observed to be higher during the rainy season than dry season in the central zone of the State when compared to other zones (Fig. 7). This could probably be informed by the effect of water run-off in mobilizing heavy metals from polluted soil and leachate, coupled with the incessant floods that occur at riverbanks during the rainy season. Our finding was in agreement with observations of previous researchers (Frazolli *et al.,* 2010; Onwughara *et al.,* 2011). From the review of Bielicka *et al.* (2005), chromium was one of the heavy metals with exaggerated concentration in the environment which is also in line with the findings of this study.

Analysis by settlement

From the result, it was observed that waterways from the urban settlement are heavily polluted with Chromium compared to waterways from the rural settlement in Kwara State (P_{cal} = 0.00, P<0.05). The elevated concentration of Chromium observed within the waterways in the urban settlement could probably be due to open method and landfilling of municipal solid waste disposal around or directly into the water bodies in majority of cities in Nigeria (Okoye and Okoye 2008; Onwughara *et al.,* 2011; Ogunkunle *et al.,* 2016). Poor e-waste disposal was documented to accounts for 70% of total heavy metals found in landfills (UNEP, 2005; Grossman, 2006; Wuhib, 2015). This was observed in cities located in the urban settlement in Kwara State since this mode of disposal is the simplest, cheapest and most cost-effective (Barrett and Lawlor, 1995).

The implication of the present findings which is in line with the observation of Wilkinson et al. (2003) is that with this worrisome level e-waste-generated heavy metals in this locality, accumulation may occur in agricultural lands making the metals readily available for uptake by grazing livestock. Continuous exposure through polluted water and soil may increase pollution of pastures with the heavy metals (Frazzoli *et al.,* 2010). According to Ogunkunle *et al.* (2016), some sampled

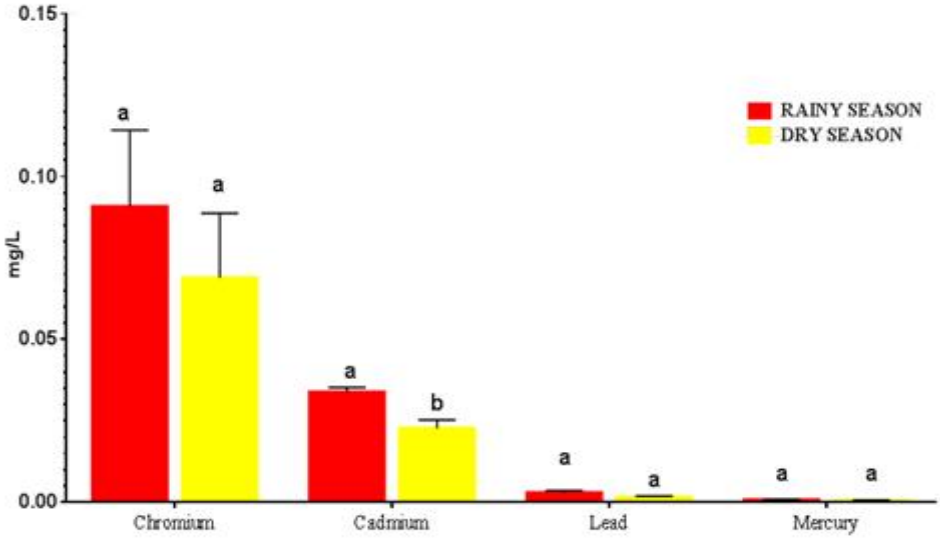

Fig. 5: Comparing heavy metals distribution by season. Data are presented as the mean ± S.E.M. p value < 0.05**.** Statistical analyses were performed by two-way ANOVA test, followed by Uncorrected Fisher's LSD test for multiple comparisons (P_{cal} = 0.482 in Chromium, P_{cal} = 0.067 in Lead, P_{cal} = 0.146 in Mercury, P > 0.05; P_{cal} = 0.001 in Cadmium, P < 0.05). Mean that do not share same alphabet are significantly different.

rivers in this study were dammed as source of portable water to the populace of Ilorin and environs while some served as major sources of fish for consumption, aquaculture and water extraction for lands irrigation especially for World Bank Sponsored Fadama irrigation program. Therefore, high level of some heavy metals recorded in this study is a source of concern for public health livestock and ecosystem. It calls for urgent attention of all the stake holders in environmental and public health management and control.

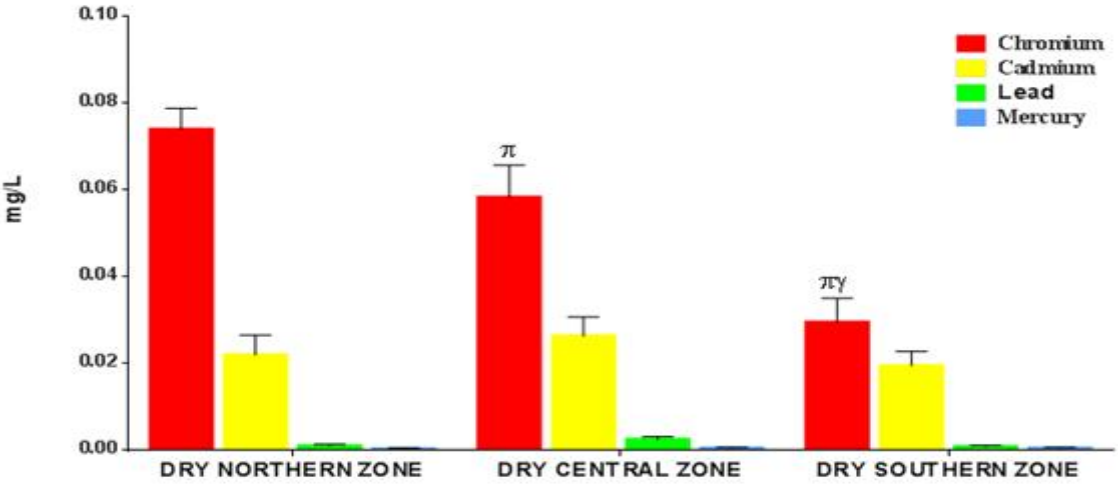

Fig. 6: Variation of mean distribution of heavy metals by geographical zones during the dry season. Data are presented as the mean ± S.E.M. p value < 0.05. Statistical analyses were performed by two-way ANOVA test, followed by Uncorrected Fisher's LSD test for multiple comparisons (P_{cal} = 0.0086 (Cr DNZ Vs Cr DCZ), P_{cal} = Â 0.0001 (Cr DNZ Vs Cr DSZ), P_{cal} = Â 0.0001 (Cr DCZ Vs Cr DSZ), P < 0.05).$^{\delta}$ p versus dry northern zone group, ^{a} p versus dry central zone group.

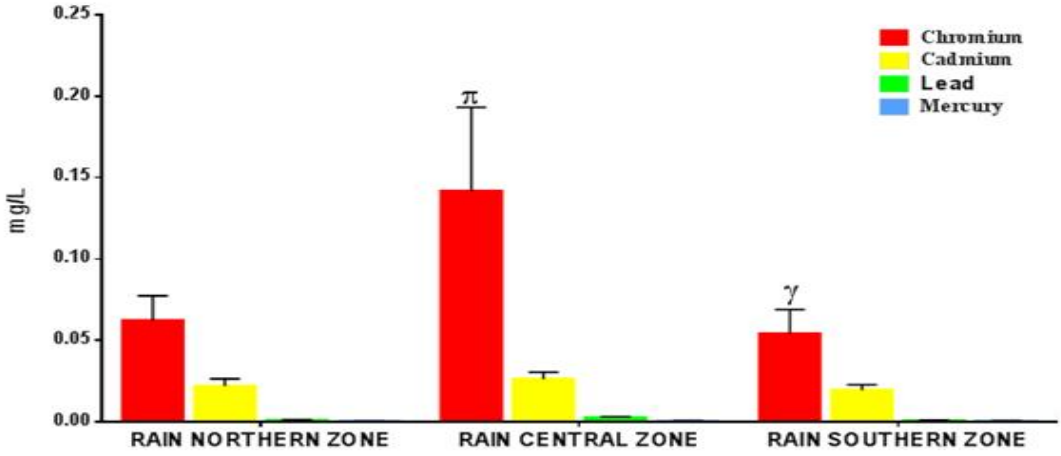

Fig. 7: Variation of mean distribution of heavy metals by geographical zones during the rainy season. Data are presented as the mean ± S.E.M. p value < 0.05. Statistical analyses were performed by two-way ANOVA test, followed by Uncorrected Fisher's LSD test for multiple comparisons (P_{cal} = 0.0008 (Cr RNZ Vs Cr RCZ), P_{cal} = 0.0003 (Cr RCZ Vs Cr RSZ), P < 0.05). $^{\delta}$ p versus rain northern zone group, ^{a} p versus rain central zone group.

CONCLUSION

Findings from this study depicted the presence of Chromium, Cadmium, Lead and Mercury in the waterways although most of the water samples appeared apparently clean, portable and hygienic for consumption. This study also revealed a significantly higher concentration of Cadmium with respect to seasonal variation (P_{cal} = 0.001, P ÂÚ 0.05) when compared to densities of Lead, Mercury and Chromium (P_{cal} = 0.482 in chromium, P_{cal} = 0.067 in lead, P_{cal} = 0.146 in mercury) during the same period. Mean concentrations of Chromium (0.318 ± 0.04) and Cadmium (0.045 ± 0.01) within the sampled waterways exceeded the maximum permissible standards (0.05mg/L for Chromium and 0.003mg/L for Cadmium) specified by (NIS, 2007) and (WHO, 2011) respectively for drinking water. Judging the frequency of the identified heavy metals by geographical zones in season showed density of Chromium to be higher. Contamination of heavy metals was also recorded to be higher in the urban areas than the rural areas.

ACKNOWLEDGEMENT

The authors acknowledge the contribution of Mr. Timothy Samson during our reconnaissance visit to the study area and Dr. Biola Kazeem Badmos for helping with the GIS. The authors also appreciate the contributions of the reviewers.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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