

TOTAL METALS IN UNIVERSITY OF LAGOS WETLANDS AND SEDIMENTS AND THEIR SPATIAL DISTRIBUTION

*Kehinde Sowunmi, Soyebo Titilayo & Lukman Sowunmi

**Department of Cell biology and Genetics, University of Lagos, Akoka, Yaba, Nigeria
Department of Applied Science, Ladoke Akintola University of Technology, Ogbomoso, Nigeria*

Abstract

Wetlands are carriers of metals and organic pollutants from natural and anthropogenic sources. Studies have shown that sediments are sinks for these pollutants as they carry more than 99% of the total amount of metals which are released as soluble metals into the Lagoon. The University of Lagos, located at Akoka North eastern part of Yaba in Lagos Mainland runs along a highly industrialized and residential area. This paper reports the total metal concentrations in wetland and sediment and their seasonal variations. Wetland and sediment samples were collected for two seasons in 8 sampling sites. Results showed wetland data having lower concentrations of metals as compared to sediments. Wet season had higher concentrations of metals as compared to other season. Total concentrations in wetlands were Cd (1.0-6.0), Cu (1.0-11.0), Cr (0.3-82.7), Zn (2.7-65.0) and Pb (0.3-16.0) all in $\mu\text{g L}^{-1}$ respectively. Statistical analysis showed that there was a significant difference between the wet and dry seasons for sediments. Cd was the only metal at acceptable levels while Cr, Cu, Pb and Zn concentrations all exceeded levels deemed acceptable by the SABS and the EPA. Therefore, the wetland is in poor health.

Keywords: heavy metals, seasonal variability, pollution, industries

1. Introduction

Heavy metals, such as lead and cadmium are considered pollutants because of their potential toxicity to plants, animals and human life (Banerjee *et al.*, 2012). Anthropogenic and natural activities, from the surrounding environment are the main sources of river pollution (Kankılıç *et al.*, 2013; Mutia *et al.*, 2012). Direct influxes from industrial and agricultural activities are common and may be further supplemented by natural weathering. Physical parameters of wetlands and sediments are pH, redox, electrical conductivity, dissolved oxygen and temperature. These contribute to the availability of heavy metals in the lagoon system, and these parameters are often included in various guidelines to monitor and control anthropogenic pollution of wetlands. Metal concentration and physical parameters are compared to wetland quality guidelines to protect the ecosystem (Farkas *et al.*, 2007). The rate of water pollution varies seasonally, depending on discharge, flow rates and interactions with the environment (Tsai *et al.*, 2007; USEPA, 2001). Seasons in Nigeria may be classified as dry or wet; the dry seasons. Studies have shown that wetlands and sediments have varying concentrations per season depending on the type of pollution and region (Kamau *et al.*, 2008; Lokeshwari *et al.*, 2006). Water usually shows high concentrations of metals during the dry season as there is no rapid movement, mixing and/or dilution caused by rainfall. In the dry season water levels reduce due to lower rainfall and evaporation, and precipitation of the metals leads to sediments accumulating most of the metals. Conversely during wet season, previously accumulated metals are released as a result of increased water flow, this is dependent on the physico chemical conditions present in the lagoon (Kamau *et al.*, 2008).

The University of Lagos situated within Lagos Mainland LGA of Lagos state lies between latitude 03.2343°E - 03.34554°E and longitude 06.2135°N - 06.4323°N. This area is host to many activities which are industrial (paint, machinery, and waste management) and agricultural (arable and livestock farming) based; these make extensive use of natural water resources. Water in the area is also used for recreational

and domestic purposes. The aforementioned industrial activities are possible sources of heavy metals particularly (Cd, Cr, Cu, Pb and Zn) contamination (Fatoki *et al.*, 2002).

Investigations on organic pollutants within the system have previously been conducted while metal determination studies have been very limited and are not widely documented for possible pollutant inputs (Barratt, 2002; Dickens *et al.*, 1998; Ramjatan *et al.*, 2000).

One study was carried out in the Olifants River for a period of one year. The results showed high concentration of Zn, Pb and Cr accumulated in different fish species at varying localities (Coetzee *et al.*, 2002). The river had industries and sewage treatment works alongside it which were reported to affect its water quality. Okonkwo and Mothiba (2005) conducted a study on trace metals from Dzindi, Madanzhe and Mvudi rivers in South Africa. The concentrations of Cd and Pb among other measure metals exceeded the international guideline for drinking water (Okonkwo *et al.*, 2004). This study measures the total concentrations of metals in the University of Lagos wetlands and sediments. A range of metals were screened in both water and sediment samples and Cd, Cr, Cu, Pb and Zn were selected based on their toxicity, essentiality and detectability in samples. Arsenic and mercury for example, while highly toxic, were present at levels below the detection limits and hence were excluded from the list of the studied metals.

2. Materials and Methods

2.1 Study Area

The University of Lagos also called UNILAG, situated within Lagos Mainland LGA of Lagos state lies between latitude 03.2343°E - 03.34554°E and longitude 06.2135°N - 06.4323°N. It is bounded on the north by Bariga, at the south by Onike and Iwaya, the east by Lagos Lagoon and at the west by Yaba.

The University of Lagos is an institution of higher learning founded in 1962. It presently has three campuses in Yaba and Surulere. The main campus which is of interest in this research is located at Akoka North eastern part of Yaba in Lagos Mainland LGA. It is largely surrounded by the scenic view of the Lagos Lagoon and with an area of 802 acres of land.

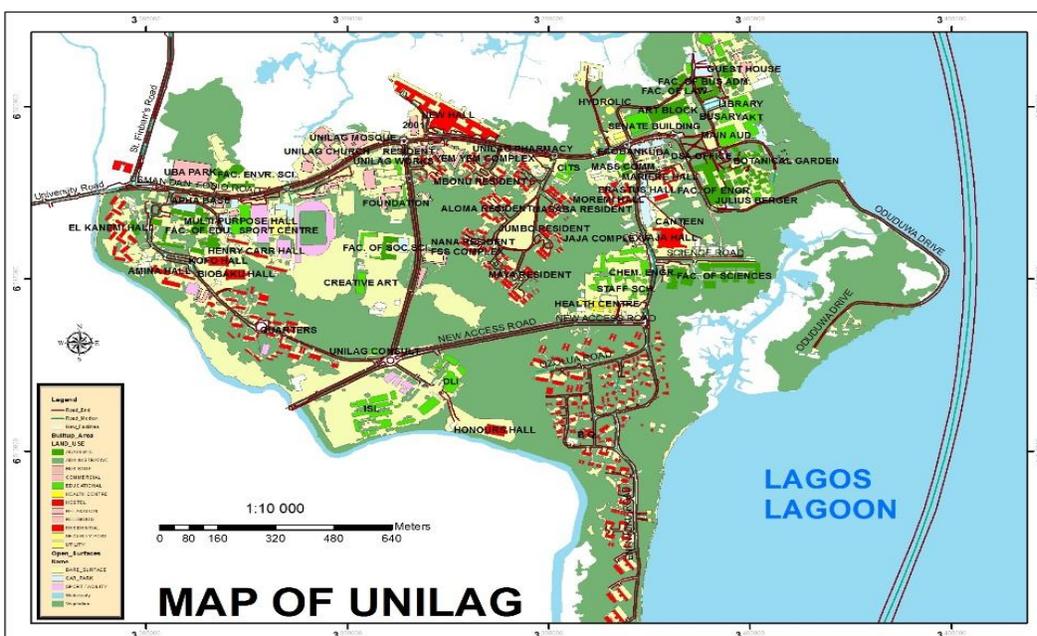


Figure 1: Existing digital map of UNILAG (Source: Department of Geography, university of Lagos.)

2.2. Experimental

This section encompasses the chemicals and instruments used in analysis of metals in wetlands and sediments.

2.2.1. Chemicals

The following chemicals were used; Nitric acid $\geq 69\%$ (Merck), Hydrochloric acid $\geq 37\%$ (Merck), 1000 ppm Cd standard (DLD Scientific), 1000 ppm Cr and 1000 ppm Pb standards (Fluka), 1000 ppm Cu and 1000 ppm Zn standards (Merck). Certified reference material NIST 2702 was from the NIST, Canada. Double distilled water was used throughout the study as blank and for making up standards and sediment samples.

2.3. Instrumentation

This involves all the apparatus that were used including the ICP-OES and microwave.

2.2.1. Microwave

Microwave digestion was done with a pressurized microwave (MARS 6, CEM) equipped with rotor that holds the vessels.

2.2.2. Inductively Coupled Plasma- Optical Emission Spectroscopy (ICP-OES)

Analysis of Cd, Cr, Cu, Zn and Pb was done using ICP-OES (Perkin Elmer, Optima 5300DV). The elements wavelengths were optimised in the instrument before calibration. These were Cd: 214.440; Cr: 283.563, Cu: 327.393, Pb: 220.353, Zn: 213.857 nm. Blanks and standards were used for calibration at the accepted correlation coefficient of greater than 0.995.

2.4. Sampling and procedure

Water samples were collected in pre cleaned polyethylene bottles and preserved with 0.5 mL concentrated HNO₃ on site and put in an ice box (Singh *et al.*, 2005). They were refrigerated at 4°C before analysis in the laboratory. Surface sediment samples were collected using a plastic scoop and placed directly into plastic bags and air dried.

Water samples were filtered through a 0.45 μm filter and analysed using Perkin Elmer ICP-OES. The dried sediment samples were ground using a pestle and mortar and sieved to 90 μm and stored in plastic bags before analysis.

The sediment samples and certified reference material were oven dried overnight at 60 °C to ensure complete dryness. Approximately 0.5 g of the sample was weighed into a microwave vessel. The samples were acid digested in the vessels using 10 mL aqua regia 1:3 (HNO₃: HCl) using MARSXpress, CEM microwave.

The microwave was set to ramp to 180 °C for 15 minutes, hold at 180 °C for 15 minutes and cool for 15 minutes. The vessels were allowed to cool at room temperature to further reduce the pressure as part of the operation procedure to avoid leaking of the solution. Elemental analysis was made using ICP-OES. Statistical analysis was done using Microsoft Excel and Statistical Package for Social Scientists (SPSS) version 18.

3. Results and discussion

Results show the certified reference material recoveries and total metals in water and sediments.

3.1. Quality assurance

Certified reference materials were used for quality assurance. Table 1 shows experimental values as compared to certified values and the relative percentage recovery. Percentage recovery of metals between 80-120% are generally acceptable (FAO, 2011; USEPA, 2012a).

Table 1: Experimental values for concentration of metals as compared to certified values and percentage recoveries *n*

Analyte name	Experimental concentration (mg kg ⁻¹)	Certified value (mg kg ⁻¹)	% Recovery
Cd	0.975 + 0.12	0.817 + 0.011	119 + 14

Cr	281 + 5.0	352 + 22	80 + 1.5
Cu	107.7 + 1.1	117.7 + 5.6	92 + 0.96
Pb	107 + 3.5	132.8 + 1.1	81 + 2.6
Zn	449.7 + 11	485.3 + 4.2	93 + 2.2

n (number of replicate analysis of the certified reference material)= 3

The percentage recoveries are within the accepted range hence it validates the procedure for the metal analysis (Table 1).

3.2. Total metals in wetlands

Water typically has lower metal concentrations compared to sediments. This is due to constant mixing and flow (Mutia *et al.*, 2012). This trend was also observed in the university wetlands, wherein the concentration of metals are lower than 0.100 mg L⁻¹ with Cd, Cr, Cu and Zn below the detection limit at some of the sites. The ranges for these metals are Cd (1.0-6.0), Cu (1.0-11.0), Cr (0.3-82.7), Zn (2.7-65.0) and Pb (0.3-16.0) all in µg L⁻¹.

3.2.1. Cadmium, Chromium and Lead

These three metals showed the highest concentrations during winter. Thus, winter as the dry season usually has the highest concentration of metals because there are no dilutions from rain (Lokeshwari *et al.*, 2006). Autumn is also classified as a dry season but unlike winter dry season; there were rains during the sampling period. The SABS value from DWAF for Cd is 150 µg L⁻¹ and from EPA is (8.8 µg L⁻¹) (DWAF, 1996b; FDEP, 2013). All the sites for Cd are below SABS limit indicating it is in the permissible level. Though Cd has a lower concentration, it is still a toxic element and not essential to aquatic life (Fianko *et al.*, 2007). Autumn and summer samples showed fluctuations with sites A, C and H in autumn having Cd below the detection limit. Generally no specific spatial trend was observed in winter and spring concentrations especially at the upper catchment.

The SABS accepted value for Cr is 7.0 µg L⁻¹ and the respective EPA value is (50.0 µg L⁻¹) (DWAF, 1996b; FDEP, 2013). All sites exceed the SABS limit in winter but other seasons are below the standard (Figure 2). Compared to the EPA standard, autumn, spring and summer are below the limit and sites B, D, E and G also exceed this limit. Mutia *et al* (2012) reported that high concentration of metals in surface water indicates that the pollution is recent, as the water exhibit high mobility (Mutia *et al.*, 2012). Thus high winter values indicate that there was a recent input of Cr into the river at the start of industries. The industries most likely responsible for the elevated Cr concentration may be chemical and textile.

Pb in B (autumn) was below the detection limit, all sites for all seasons are exceeding the SABS limit and also exceed the EPA limit in the winter season. The SABS limit is 0.2 µg L⁻¹ while the EPA is (8.5 µg L⁻¹) (DWAF, 1996b; FDEP, 2013). Seasonal variation shows winter having the highest concentration in all sites except A and H in summer.

3.2.2. Copper and Zinc

Cu and Zn showed distinct seasonal fluctuations. Wet season had the highest concentration among other seasons. Sites exceeded the SABS Cu limit of (0.3 µg L⁻¹) (DWAF, 1996b) except for A, B, C and H in wet season which had concentrations below the detection limit. All sites were below the EPA limit which is (3.7 µg L⁻¹) (FDEP, 2013).

Zn does not follow any seasonal or spatial trend, but its concentrations compared to the SABS limit all sites exceeded the recommended limits except sites A and B (dry season) which were below detection limit. Figure 2 shows concentration of Zn in all sites compared to the SABS values. Comparing the concentration of Zn in samples to the standards of 2.0 µg L⁻¹ and 86 µg L⁻¹ for SABS and EPA respectively, all sites had concentration below the SABS and EPA standards (DWAF, 1996b; FDEP, 2013).

Most sites are above the stipulated limit, thus the ecosystem of the university of Lagos wetland may have been negatively affected by the various activities around it. These metals may be from natural sources especially in the upper catchment immediately from industries in the lower catchment. The waste

management plant receives waste-water from households and industries which is treated and disposed into the lagoon. The input of pollutants from the waste management brings a change to the dynamics of the metals in the lagoon. The water discharged is not free from pollutants, as the concentrations in those areas are very high. This is observed in the three preceding sites; thus it explains the increase in concentration of metals just after the connection with the waste management. Moreover, in autumn and winter there was construction at H and it is observed that there is high concentration of Pb, Cu and Zn in that area for dry season.

Table 2: Average total concentrations for wetlands data

Site code	Seasons	Wet		dry
A	Cd	<DL	0.0027	0.0020
	Cr	<DL	<DL	0.0003
	Cu	<DL	0.0087	0.0097
	Mn	0.0327	0.1257	0.1777
	Pb	0.001	0.0033	0.0083
	Zn	<DL	0.0237	0.0157
B	Cd	0.0020	0.0020	0.0020
	Cr	<DL	0.0057	<DL
	Cu	0.0090	<DL	0.0020
	Mn	0.0930	0.0380	0.1996
	Pb	<DL	0.0010	0.0023
	Zn	0.0290	0.0173	0.0027
C	Cd	<DL	0.0013	0.0013
	Cr	<DL	0.0040	<DL
	Cu	0.0007	0.0010	0.0010
	Mn	0.0867	0.0537	0.0346
	Pb	0.0003	0.0003	0.0010
	Zn	0.0123	0.0177	<DL
D	Cd	0.002	0.0010	0.0017
	Cr	0.001	0.0040	<DL
	Cu	0.0050	0.0067	0.0010
	Mn	0.0830	0.0710	0.0463
	Pb	0.0010	0.0003	0.0007
	Zn	0.0130	0.0290	0.0067
E	Cd	0.002	0.0010	0.0017
	Cr	0.002	0.0033	<DL
	Cu	0.0120	0.0013	0.0013
	Mn	0.1800	0.0766	0.0866
	Pb	0.0050	0.0030	0.0017
	Zn	0.0060	0.0277	0.0077
F	Cd	0.0010	0.0020	0.0013
	Cr	0.0020	0.0043	0.0033
	Cu	0.0050	0.0307	0.0110
	Mn	0.1880	0.1517	0.1033
	Pb	<DL	0.0063	0.0017
	Zn	0.0150	0.1953	0.0596
G	Cd	0.0020	0.0020	0.0017
	Cr	0.0030	0.0010	0.0003

Cu		0.0070	0.0053	0.0030
Mn		0.2320	0.1030	0.1030
Pb		0.0030	0.0030	0.0020
Zn		0.0170	0.3130	0.0103
H		0.0020	0.0017	0.0020
	Cd			
Cr		0.0030	0.0013	0.0030
Cu		0.0080	0.0063	0.0110
Mn		0.2330	0.1050	0.1663
Pb		0.0040	0.0056	0.0160
Zn		0.0150	0.0313	0.0290

<DL: Below Detection Limit

3.3. Total metals in sediments

Total metals refer to individual concentrations of metals in the sediments and their measurement plays an important role in the environment. They indicate the level of pollution by providing individual concentrations at different sampling points (Divvela, 2010). High concentrations of metals accumulate in the sediments, and later be dispersed into the environment. Therefore, this study investigates the concentrations Cd, Cr, Cu, Pb and Zn to determine toxicity and seasonal variability. Statistical analysis for variability of sediment was done using one-way ANOVA.

The significant differences were between the dry season and the wet season hence the data presented will show the lowest amount of rainfall received, representing the dry season and the highest rainfall will represent the wet season. After the wet season, the turbidity decreases due to reduced mixing from rainfall; hence metal concentrations decrease in the dry season as metals have been washed away. The spatial distribution of each of the metals shows the trend at which the metal was following from the upper catchment till the lower catchment. There is no Nigeria sediment guideline therefore the EPA standard was used to determine if metal concentrations were within the acceptable limit (Gordon *et al.*, 2010).

3.3.1. Cadmium

There were high values of Cd in the wet season hence there is higher input in the wet season than in the dry season. Wet season showed Cd concentration below the detection limit $0.1 \mu\text{g L}^{-1}$ (PerkinElmer, 2008) in D, E, F and G. Low concentrations were expected during dry season because of lower rainfall. **Table 3** shows a comparison of sites to the EPA guideline value of 0.676 mg kg^{-1} ; all concentrations obtained for Cd in dry season exceeded the limit. Sites A, C, F and H in wet season also exceeded the EPA limit

Table 3: Cd concentration (mg kg^{-1}) in sediments compared to the EPA guideline value, $n=3$

	A	B	C	E	F	G	H	
Dry	133.84 (± 0.92)	166.40+ 0.37	117.34+ 1.4	199.22+ 0.41	207.91+ 1.8	351.36+ 0.79	156.10+ 1.3	191.5 7+ 1.1
Wet	*0.23+ 0.42	1.98+ 0.32	5.23+ 1.7	*0.00	*0.00	*0.00	*0.00	*0.46 + 0.17
EPA	0.676	0.676	0.676	0.676	0.676	0.676	0.676	0.676

(Standard deviation), *Below EPA limit

Cd concentrations showed fluctuations at the upper catchment of the wetland, especially in the wet season, with an increase at the settlement to industrial zone. The wet season showed an increased input of Cd at the industries; E and F had an increase in concentration. The increase in concentration of Cd at F reflected that

inputs of Cd are likely to be from the waste management plant or domestic waste entering from the informal settlement. Concentration of Cd may be due to concentration effects from inputs of discharge from industries, landfills and use of fertilizers. Use of phosphate fertilizer in agriculture may pollute the river as Cd binds into organic matter, phosphate, sulphate, hydroxide and carbonate (Fianko *et al.*, 2007).

It is stated that Cd may be adsorbed into sediments immediately or be transported in aqueous solution to a distance of 50 km and later settle back into the sediments (Friberg *et al.*, 1992). It can be assumed that Cd from the upper sites settled in the estuarine site as the water is almost stagnant. The wetland may be impacted by industries along it such as battery, steel and paint industries which are sources of Cd. The high concentration of Cd accumulated in sediments to the aquatic life as Cd is a toxic metal. The possible impacts of this high Cd concentration on humans are brain damage and pains in the bones (Fatoki *et al.*, 2002). These happen when Cd is released from sediments in dissolved form into the wetland and taken up by fish and other aquatic animals which are then consumed by humans.

3.3.2. Lead

Spatial distribution shows the industrial sites having lower amount of Pb as compared to the upper catchment. This suggests that the pollution in that area was anthropogenic. It may be from chemical weathering during high temperatures in the wet season releasing Cd (Dekov, Komy, Araújo, *et al.*, 1997). Compared to the EPA limit 30.2 mg kg⁻¹; spring and summer had high concentration of Pb which exceeded the EPA limit, whereas in autumn and winter, concentrations were low and were below the limit as shown in Figure 3. The concentration of Pb in A, B, C, D, E and F in autumn and winter were below the EPA stipulated limit.

The spatial distribution for Pb in the wet season shows high concentrations in A, then fluctuation in D. Sources of Pb along wetlands may include paint and battery manufacturing present along the lagoon at the start of industries (Agarwal, 2009). Agricultural activities may also contribute to the concentration of Pb at the start of industries as Pb is found in some fertilizers (Maroulis *et al.*, 2007; McLaughlin *et al.*, 1996). The minor increase in Pb concentration in F may be due to the waste management plant or the informal settlement located near the area. The effluent discharge from the waste plant and the runoff from the settlement may increase the concentration of Pb (Fatoki *et al.*, 2002).

Closer to the informal settlement there is litter composed of cans and other metal materials which rust and may have added to the amount of contamination. When deposited in solid form such as ash, few Pb compounds readily dissolve in water but will be precipitated as solid into sediments. Generally the industrial site has lower concentrations and only an immediate increase at H. Wright *et al.* (1999) explained this increase that high concentrations of metals in estuaries are caused by the feeding lagoon and direct discharges (Wright *et al.*, 1999). It could therefore be expected that Pb from the upper catchments was trapped in the estuary and accumulated in the sediments, or may be as a result of construction works.

Table 4: Average total concentrations for sediment data

Site code	Seasons	wet	Wet	Dry	Dry

A	Cd	1.32	0.23	197.39	133.84
	Pb	12.87	12.13	536.75	601.70
	Cu	13.47	16.13	84.72	106.02
	Cr	57.75	51.75	67.07	94.16
	Zn	62.25	81.95	104.05	89.75
	Mn	537.39	632.76	80.83	89.87
B	Cd	0.07	1.98	126.00	166.40
	Pb	19.62	20.88	430.79	205.60
	Cu	22.87	27.11	82.54	118.01
	Cr	72.46	83.50	54.04	48.93
	Zn	109.95	95.75	61.94	60.86
	Mn	5012.82	9822.15	46.70	62.45
C	Cd	1.25	5.23	164.67	117.34
	Pb	21.07	27.07	528.37	525.83
	Cu	33.03	11.86	62.22	114.54
	Cr	86.27	135.06	45.92	28.61
	Zn	80.57	73.47	82.90	29.51
	Mn	1040.02	2189.52	45.50	56.53
D	Cd	0.18	<DL	250.79	199.22
	Pb	15.28	22.51	304.21	95.39
	Cu	21.00	24.92	165.71	105.81
	Cr	57.39	78.95	78.14	88.50
	Zn	84.41	77.96	80.43	92.41
	Mn	474.74	687.58	72.83	62.87
E	Cd	0.20	<DL	264.46	207.91
	Pb	55.04	28.60	225.54	256.21
	Cu	37.55	21.75	154.26	67.99
	Cr	81.94	60.86	91.99	63.62
	Zn	176.50	103.89	96.90	81.31
	Mn	499.54	497.57	81.11	64.18
F	Cd	0.73	0.99	205.18	151.81
	Pb	136.13	53.82	186.02	144.73
	Cu	133.49	81.21	128.53	119.99
	Cr	126.35	111.94	98.14	102.86
	Zn	602.12	246.20	57.98	103.25
	Mn	737.18	1052.19	48.60	85.70
G	Cd	0.13	<DL	207.90	351.36
	Pb	65.88	28.81	211.16	266.26
	Cu	80.88	132.99	123.95	123.01
	Cr	127.45	55.08	82.71	116.10
	Zn	420.65	469.92	59.20	146.33
	Mn	649.32	284.25	54.80	117.70
H	Cd	<DL	<DL	211.95	156.10
	Pb	51.15	32.98	174.83	212.95
	Cu	65.97	118.92	164.00	168.47
	Cr	98.83	52.17	105.36	122.31
	Zn	262.63	339.37	81.24	131.85
	Mn	472.56	389.46	82.09	107.57

<DL: Below Detection Limit

4. Conclusion

The concentration of Cd, Cr, Cu, Pb and Zn in wetlands and sediments, seasonal variations and their distribution along the Lagoon has been found. Concentrations were compared to the SABS and EPA wetland and sediment quality guidelines. Wetland data showed Cr, Cu, Zn and Pd above the stipulated SABS limit while for sediments Cd, Cr, Cu, Pb and Zn were above the EPA limit. In the wet season Cd in

water was below the SABS limit and above for sediments. Based on this, use of water directly from the lagoon may pose health problems like kidney disease, bone disease, brain damage and other illnesses (Fatoki *et al.*, 2002).

The results showed there was a significant difference in concentration of metals in sediments between the dry seasons and the wet seasons. The study shows a variation in the amounts of metals at different sampling points due to varying types of activities along the lagoon. The spatial distribution showed an increase in concentration of Cd, Cr, Cu, Pb and Zn at the start of industries moving down to the end of industries, with Cd, Cr and Pb mostly at the estuarine site; ES. Construction was conducted near site H during these seasons which ceased before dry season hence detectable in the wet seasons, this may have been due to dredging of sediments from the land. The upper catchment which is A to C shows an increase in concentration of Cd, Cr, Cu and Pb in the dry season but a decrease in the wet season. Unlike other metals; Zn showed a decrease from A to C but only in the wet season with fluctuations in the dry seasons. Most of the metals increase in concentration at the waste management facility and decrease down the preceding sites. Sediment samples particularly those taken during the wet season showed the highest levels of contamination while the water showed a peak in contamination during the dry season. The highest contamination is in the residential site. Generally the river shows that it is in poor health as most of the metals in water and sediment are exceeding the SABS and EPA limits respectively. There is a need for increased environmental monitoring along the University of Lagos wetlands.

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Conflict of interest

The authors declare no competing interest

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