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Research Article

Heavy Metals Contamination in Water, Soil and Plant Samples of Okomu National Park, Edo State, Nigeria.

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ABSTRACT

The pollution of the environment with a wide range of contaminants has become a matter of great concern over the last few decades. Heavy metals are considered to be one of the main contaminants in the environment, since they have a significant effect on ecological quality. They have the capability to move from contaminated soils and water and bioaccumulate in plant species that herbivores ingest causing health risks to various organisms in the food chain as a result of bioaccumulation. This study therefore assessed the levels of heavy metals in water, soil and plant samples of Okomu National Park, Edo State, Nigeria. Water samples were collected by grab sampling while top soil (0-15 cm) and plant samples were collected randomly. Samples of water (8), soil (8) and plant (6) were collected for two seasons (dry and wet) and analysed for heavy metals: Copper (Cu), Nickel (Ni), Chromium (Cr), Zinc (Zn), Iron (Fe), Lead (Pb), Manganese (Mn) and Cadmium (Cd) using Atomic Absorption Spectrophotometer after wet (acid) digestion. Data collected were subjected to descriptive (mean, standard deviation) and inferential (T-test) statistics using Statistical Package for Social Sciences with statistical significance set at $\alpha_{0.05}$. The mean values of heavy metals in the water samples revealed that all the heavy metals analysed (except Cu and Zn) were above the WHO guidelines for drinking water. The level of Cd in the soil samples was higher than the comparable maximum allowable limit while the mean values of all the analysed heavy metals (except Zn) in the sampled plant species were above the comparable WHO permissible limit. Significant seasonal variation in the concentration of heavy metals was observed in the study as there was more metal contamination in all the analysed samples during the wet season. The concentrations of analysed heavy metals and influence of seasonal variation observed in this study may have negative implication on wildlife health within Okomu National Park. As such, there is need to carry out the study (in sediments inclusive) over time so as to monitor heavy metal deposition and route of exposure in the park.

Keywords: Heavy metals contamination, seasonal variation, Okomu National Park, Nigeria.

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INTRODUCTION

The study of the environment and its constituents thereof has been on-going for centuries and the chemical composition of naturally-occurring environmental variables keep changing according to the climatic and atmospheric conditions of the biosphere (Shalini *et al*., 2017). The pollution of the environment with a wide range of contaminants has become a matter of great concern over the last few decades (Al-Weher, 2008). The availability and significance of these contaminants in the air, soil or water is fast contributing to poor environmental health. Heavy metals are considered to be one of the main contaminants in the environment, since they have a significant effect on ecological quality (Omonona *et al*., 2019a). Though there is no consensus definition of heavy metals within the literatures, density, atomic weight and degree of chemical toxicity are generally being used in describing heavy metals with modes of exposure to include inhalation, ingestion and dermal contact absorption (Xiong and Yanxia, 2010). The two main sources of heavy metal concentration are natural and anthropogenic contamination. Natural sources include parent rocks and metallic minerals (metalliferous ores) while anthropogenic sources include agriculture (fertilizers, animal manures, pesticides), metallurgy (mining, smelting, metal finishing), energy production (leaded gasoline, battery manufacture, power plants), microelectronics, and sewage sludge and scrap disposal (Adriano, 2001). The latter has been noted to have significant influence on the increased levels of environmental metal concentrations (Shalini *et al*., 2017).

The increasing world production and subsequent common usage of heavy metals has facilitated expanded interest in the field of heavy metal research (Marjanovic *et al*., 2009). The problem with heavy metals is their persistence, making it impossible to eliminate them from the environment (Adetuga, 2019). Knowing that the concentration of metals within the environment is valuable for many scientific disciplines, it is most important to understanding the relationship between the total concentration of metals and their biological effects (Ratko *et al*., 2011). Heavy metals have been introduced into rivers through land surface runoff, rainfall precipitation and factory waste discharges (Ahmad *et al*., 2009) while atmospheric deposition has been a major mechanism for metal input to plants and soils (Sparks, 2005). Heavy metals have the capability to move from contaminated soils and water and bioaccumulate in plant species that herbivores ingest causing health risks to various organisms in the food chain as a result of bioaccumulation (Khan *et al*., 2008). Heavy metal toxicity is frequently the result of long-term, low-level exposure to common pollutants in our environment (Shalini *et al*., 2017). Exposure to toxic heavy metals is associated with many chronic diseases and can cause a wide variety of health problems. Ecological health is somewhat dependent on plants (vegetation) and the abiotic components of the environment (water, soil and air). When any of these is contaminated, there is high possibility of a resultant effect on wild animal health which can pose severe threats to wild species population and perpetuation. This study therefore assessed the levels of heavy metals in water, soil and plant samples of Okomu National Park, Edo State, Nigeria.

MATERIALS AND METHODS

Study Area: Okomu National Park (ONP) previously known as the Okomu Wildlife Sanctuary is the smallest national park in Nigeria with a land area of 212 km^2. (Plate 1). It was established by decree 46 of 1999 and lies between coordinates 6^{o} 10′ - 6^{o} 30′ N and 5^{o} 00′ - 5^{o} 30′ E (Onojeghuo and Onojeghuo, 2015). The mean annual rainfall of the park is about 2100 mm while the mean monthly temperature is 30.2^{o}C. The soils of the park are acidic sandy loam derived from deep deltaic and coastal sediments (Soladoye and Oni, 2000) with a gentle topography ranging from 30 m to 60 m above sea level. The park is an important refuge for forest white-throated monkey (*Cercopithecus erythrogaster*) which is an endemic species in Okomu National Park. Other endangered wildlife species of local and global concern such as the forest elephant (*Loxodonta africana cyclotis*), chimpanzee (*Pan troglodytes versus*), leopard (*Panthera pardus*) and Red-capped Mangabey (*Cercopithecus torquatus*) are also found in the park (Ajayi, 2011). The park is also rich in tree species such as *Entandrophragma angolense, Lovoa trichilioides, Anopyxis klaineana, Nauclea diderrichii* and *Diospyros crassiflora*..

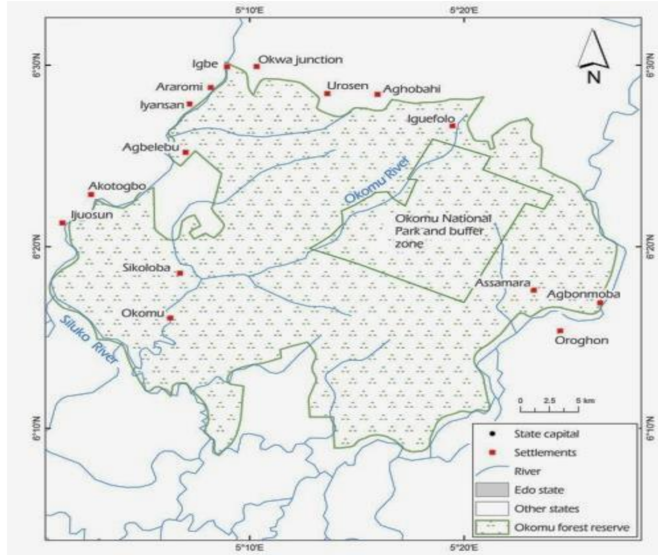

Plate 1:
Map of Okomu National Park showing the Okomu River and the surrounding settlements

Samples Collection and Technique: Water sampling at four sampling stations (Agekpupu River, Arakhuan Stream, Lake 52 and Okomu River) was performed using the grab sampling technique. Water samples were collected (from the upper, middle and lower courses of each waterhole and composited) into self-cleaned sample bottles that were adequately labelled. For soil sampling, soil samples of the top soil (0 – 15 cm depth) were collected randomly at four points within the park using a hand-held auger into clean self-sealed polyethene bags that were well-labelled appropriately. For plant sampling, three plant species were randomly collected at different points within the park based on the utilization preference by the herbivores and subsequently transported to the laboratory for analysis. These plants are *Diaplazea supericapa* (Elephant okra), *Cola smithii* (Monkey kola) and *Dioscorea prehensilis* (wild yam). All samples [water (n=8), soil (n=8), plant (n=6)] were taken to the laboratory after collection and assessed for heavy metal exposure. Samples collection were done between February and June, 2018 with the assistance of park rangers covering two seasons (dry and wet) so as to evaluate the impact(s) of seasonal variation on heavy metal levels.

Selected Heavy Metals and Laboratory Analysis: Heavy metals such as Copper (Cu), Nickel (Ni), Chromium (Cr), Zinc (Zn), Iron (Fe), Lead (Pb), Manganese (Mn) and Cadmium (Cd) were analysed in all the samples. These heavy metals were purposively selected because they constitute part of the eleven heavy metal elements of highest wildlife protection concern (Beyersmann and Hartwig, 2008). For water sample analysis, about 50 ml of the water samples were taken at each sampling station and acidified with 10% HNO_3 immediately in order to prevent analyte loss and thereafter placed in an ice bath and taken to the laboratory where they were transferred into 250 ml beakers and properly digested using wet acid digestion method. For soil sample analysis, approximately 1 gm of each soil sample was air-dried, pulverized with an agate mortar and then sieved through a nylon sieve (a pore diameter of less than 0.149 mm). About 0.5 g of dried homogenized soil samples was weighed and digested in a Teflon beaker with a mixture of HNO_3, $HClO_4$ and HF in the ratio 4:1:4 respectively (Asaolu, 2003). The mixture was thereafter heated for three hours at 85ºC while the digest was then filtered into 100 ml standard flask and made up to mark with deionized water. For plant sample analysis, plant samples were oven-dried at 60^{0}C and pulverized with a pulverizer. Then, about 1.0 g of each dried plant sample was appropriately digested in a mixture (3:1) of concentrated nitric acid and hydrofluoric in microwave-assisted Kjeldahl digestion process. The digestion process was repeated until the digested solution became clear. Sequel to complete digestion, all the samples were subjected to heavy metals determination using the Atomic Absorption Spectrophotometer (AAS) at specific wavelengths for each of the heavy metals.

Statistical Analysis: Data collected were presented and expressed as Mean ± Standard Deviation and subjected to T-test. Statistical significance was set at $\alpha_{0.05}$. All statistical analyses were done using IBM Statistical Package for Social Science (SPSS, version 20.0)

RESULTS

Heavy metal levels in the water samples: The result showed that the levels of Fe and Mn in the sampled waterholes were above the WHO guidelines for drinking water while other analysed heavy metals were below the WHO guidelines for drinking water during the dry season as shown in Table 1. Furthermore, in the wet season as exemplified in Table 2, the levels of Ni (in Okomu River), Cr, Fe, Pb (except in Agekpupu River), Mn and Cd were above the WHO guidelines for drinking water while Cu, Ni (except in Okomu River) and Zn were below the comparable WHO guidelines for drinking water. The mean levels of the analysed heavy metals in the sampled waterholes revealed that Ni (wet season), Cr (wet season), Fe (both seasons), Pb (wet season), Mn (wet season) and Cd (wet season) were above the WHO guidelines for drinking water as shown in Table 3.

Table 1:
Heavy metal levels in the sampled waterholes of Okomu National Park (Dry Season, 2018)

Water Holes	Coordinates	Cu (mg/l)	Ni (mg/l)	Cr (mg/l)	Zn (mg/l)	Fe (mg/l)	Pb (mg/l)	Mn (mg/l)	Cd (mg/l)
Okomu River	N 06o20’28.1’’; E 005o14’00.2’’	0.02	0.00	0.00	0.00	0.71	0.00	0.07	0.00
Agekpupu River	N 06o24’53.8’’; E 005o17’59.7’’	0.01	0.00	0.00	0.10	1.60	0.00	0.12	0.00
Arakhuan Stream	N 06o20’34.9’’; E 005o21’39.1’’	0.00	0.00	0.00	0.07	0.72	0.00	0.19	0.00
Lake 52	N 06o21’37.9’’; E 005o19’23.9’’	0.00	0.00	0.00	0.07	1.34	0.00	0.53	0.00

Table 2:
Heavy metal levels in the sampled waterholes of Okomu National Park (Wet Season, 2018)

Water Holes	Coordinates	Cu (mg/l)	Ni (mg/l)	Cr (mg/l)	Zn (mg/l)	Fe (mg/l)	Pb (mg/l)	Mn (mg/l)	Cd (mg/l)
Okomu River	N 06o20’28.1’’; E 005o14’00.2’’	0.05	0.16	0.14	0.01	74.00	0.04	1.76	0.01
Agekpupu River	N 06o24’53.8’’; E 005o17’59.7’’	0.03	0.01	0.12	0.01	68.00	0.01	7.68	0.01
Arakhuan Stream	N 06o20’34.9’’; E 005o21’39.1’’	0.03	0.04	0.09	0.01	43.00	0.02	1.74	0.01
Lake 52	N 06o21’37.9’’; E 005o19’23.9’’	0.03	0.07	0.12	0.01	32.00	0.12	1.76	0.02

Table 3:
Mean values of heavy metals in the sampled waterholes of Okomu National Park

Heavy metals	Mean Values ± Std. Deviation		WHO (2011) Guidelines for Drinking water
	Dry Season (January, 2018)	Wet Season (June, 2018)	
Cu (mg/l)	0.01 ± 0.01	0.04 ± 0.01	2.0
Ni (mg/l)	0.00 ± 0.00	0.07 ± 0.06	0.07
Cr (mg/l)	0.00 ± 0.00	0.12 ± 0.02	0.05
Zn (mg/l)	0.06 ± 0.04	0.01 ± 0.00	5.0
Fe (mg/l)	1.09 ± 0.45	54.25 ± 20.01	0.3
Pb (mg/l)	0.00 ± 0.00	0.05 ± 0.05	0.01
Mn (mg/l)	0.23 ± 0.21	3.24 ± 2.96	0.4
Cd (mg/l)	0.00 ± 0.00	0.01 ± 0.01	0.003

Heavy metal levels in the sampled soils

The result showed that all the heavy metals analysed in the soil samples during the dry season were below the maximum allowable limit as specified by Sweden (Table 4) except Pb (92.67 mg/kg) in SS_4 while during the wet season, Cd (in all the soil samples except SS_1) were above the maximum allowable limit as specified by Sweden. Similarly, high concentrations of Fe, Pb and Mn were also observed in the sampled soils during the wet season (Table 5) while Ni and Cd were not detected during the dry season. The mean values of the analysed heavy metals in the soil samples showed that Cd level (during the wet season) was higher than the comparable maximum allowable limit (Table 6).

Table 4:
Heavy metal levels in soil samples of Okomu National Park (Dry Season, 2018)

Soil Samples	Coordinates	Cu (mg/kg)	Ni (mg/kg)	Cr (mg/kg)	Zn (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	Mn (mg/kg)	Cd (mg/kg)
SS1	N06o24’53.5’; E005o17’59.4’	5.73	0.00	0.00	24.63	8423.50	33.70	20.99	0.00
SS2	N06o20’35’.2’; E005o21’40’.9’	6.28	0.00	22.85	18.78	6816.70	40.75	15.48	0.00
SS3	N06o21’37.5’; E005o19’24.3	5.58	0.00	17.42	14.47	520.77	47.01	182.73	0.00
SS4	N06o20’28.0’; E005o14’00.2	2.28	0.00	19.00	64.65	16319.20	92.67	31.47	0.00

Table 5:
Heavy metal levels in soil samples of Okomu National Park (Wet Season, 2018)

Soil Samples	Coordinates	Cu (mg/kg)	Ni (mg/kg)	Cr (mg/kg)	Zn (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	Mn (mg/kg)	Cd (mg/kg)
SS1	N06o24’53.5’; E005o17’59.4’	40.00	21.85	19.6	21.20	3250	45.55	215.0	0.20
SS2	N06o20’35’.2’; E005o21’40’.9’	13.20	10.45	26.25	5.90	2890	25.10	182.5	1.25
SS3	N06o21’37.5’; E005o19’24.3	43.95	22.30	28.05	14.70	1750	66.65	154.0	0.50
SS4	N06o20’28.0’; E005o14’00.2	21.95	19.76	27.18	29.10	1860	64.15	212.5	0.55

Table 6:
Mean values of heavy metals in the soil samples of Okomu National Park

Heavy metals	Mean Values ± Std. Deviation		Maximum Allowable limit (Sweden)
	Dry Season (January, 2018)	Wet Season (June, 2018)	
Cu (mg/kg)	4.97 ± 1.82	29.78 ± 14.62	100
Ni (mg/kg)	0.00 ± 0.00	18.59 ± 5.54	35
Cr (mg/kg)	14.82 ± 10.14	25.27 ± 3.85	120
Zn (mg/kg)	30.63 ± 23.06	17.73 ± 9.84	350
Fe (mg/kg)	8020.04 ± 6499.38	2437.50 ± 746.34	NA
Pb (mg/kg)	53.53 ± 26.65	50.36 ± 19.29	80
Mn (mg/kg)	62.67 ± 80.32	191.00 ± 28.75	NA
Cd (mg/kg)	0.00 ± 1.82	0.63 ± 0.44	0.4

Table 7:
Heavy metal levels in the sampled plant species in Okomu National Park **(**Dry Season, 2018)

Plant samples	Coordinates	Cu (mg/kg)	Ni (mg/kg)	Cr (mg/kg)	Zn (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	Mn (mg/kg)	Cd (mg/kg)
Diaplazea supericapa	N 09o53’51.9; E 003o59’09.9	8.72	0.00	22.40	36.97	127.72	0.00	161.97	0.00
Cola smithii	N 09o54’12.9; E 003o58’23.7	10.83	0.00	26.80	17.68	96.87	30.60	22.13	0.00
Dioscorea prehensilis	N 09o54’47.3; E 003o57’18.7	17.47	0.00	20.43	31.00	458.67	20.57	487.10	0.00

Table 8:
Heavy metal levels in the sampled plant species in Okomu National Park **(**Wet Season, 2018)

Plant samples	Coordinates	Cu (mg/kg)	Ni (mg/kg)	Cr (mg/kg)	Zn (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	Mn (mg/kg)	Cd (mg/kg)
Diaplazea supericapa	N 09o53’51.9 E 003o59’09.9	27.63	14.08	3.68	47.23	326.5	4.45	136.25	0.33
Cola smithii	N 09o54’12.9 E 003o58’23.7	21.65	13.45	0.45	16.93	418.0	3.78	149.50	0.83
Dioscorea prehensilis	N 09o54’47.3 E 003o57’18.7	17.7	12.58	2.40	12.89	291.7	14.90	127.00	0.63

Heavy metal levels in the plant samples: The result showed that the levels of Ni, Pb (in *Diaplazea supericapa*) and Cd were not detected in the plant samples during the dry season while the levels of Cr, Fe, Cu (except in *Diaplazea supericapa*), Pb and Mn (only in *Dioscorea prehensils*) were observed to be higher than the comparable WHO recommended limits as shown in Table 7. Similarly in the wet season as exemplified in Table 8, the levels of Cu, Ni, Cr (except in *Cola smithii*), Fe, Pb and Cd were found to be higher than the comparable WHO recommended limits. The mean levels of Cu, Ni (wet season), Cr, Fe, Pb, Mn (dry season) and Cd (wet season) were above the comparable WHO permissible limit as shown in Table 9.

Table 9:
Mean levels of heavy metals in the sampled plant species in Okomu National Park

Heavy metals	Mean Values ± Std. Deviation		WHO Permissible Limit
	Dry Season (January, 2018)	Wet Season (June, 2018)	
Cu (mg/kg)	12.34 ± 4.57	22.33 ± 4.99	10.0
Ni (mg/kg)	0.00 ± 0.00	13.37 ± 0.75 a	1.5
Cr (mg/kg)	23.21 ± 3.26	2.18 ± 1.62 b	1.5
Zn (mg/kg)	28.55 ± 9.88	25.68 ± 18.77	50.0
Fe (mg/kg)	227.75 ± 200.57	345.4 ± 65.23	20.0
Pb (mg/kg)	17.06 ±15.60	7.71 ± 6.24	2.0
Mn (mg/kg)	223.73 ± 238.56	137.58 ± 11.31	200
Cd (mg/kg)	0.00 ± 0.00	0.60 ± 0.25	0.3

DISCUSSION

Heavy metal contamination and accumulation is a serious problem around the world due to the toxicity, varying sources, non-biodegradable properties, and accumulative tendencies of heavy metals (Hu *et al*., 2017). Increasing exposure to these ecotoxicants in terrestrial and aquatic organisms can have adverse toxicological effects (Omonona *et al*., 2019a). Freshwater systems including rivers, streams and lakes are often contaminated due to runoff and drainage via sediments or disposal, while groundwater is impacted through leaching or transport via mobile colloids (Adriano *et al*., 2005). Discharge of heavy metals into rivers or any other aquatic environment can change both aquatic species diversity and ecosystems due to their toxicity and accumulative behaviour (Al-Weher, 2008). High Cr in the waterholes observed in the study may have resulted from the discharge of chromium-containing waste while the high level of Fe observed may be due to effluents and anthropogenic discharge of wastewaters from the surrounding communities as collaborated by Adetuga *et al*. (2018). This finding is also similar to those of Omonona *et al.* (2019a, 2019b) who reported high level of Fe in River Omo of Omo Forest Reserve and in sampled perennial waterholes of Kainji Lake National Park respectively. The level of Pb above comparable permissible limit may be attributed to industrial waste discharges (from Okomu Oil Company) and exhaust from heavy-duty vehicles. Rani and Reddy (2003) also reported high Pb content in the water samples of their study. The run-off of fertilizers, pesticides biosolids (sewage sludge) from surrounding communities may have caused the increased level of Cd above permissible guideline in the sampled waterholes as averred by Shalini *et al.* (2017). Tong and Chen (2002) had earlier reported that Cd concentrations may occur due to high degree of anthropogenic stress. The mean levels of the analysed heavy metals in the sampled waterholes revealed that Ni (wet season), Cr (wet season), Fe (both seasons), Pb (wet season), Mn (wet season) and Cd (wet season) were above the WHO guidelines or permissible limits for drinking water with possible implication of high non-potability of the waterholes. Significant seasonal variation of heavy metal levels was also observed in the sampled waterholes with wet season having higher concentration of metals. Similar observations were also reported by Adetuga *et al.* (2018) and Omonona *et al.* (2019a, 2019b).

In terrestrial ecosystems, soils are the major recipient of metal contaminants, while in aquatic systems sediments are the major sink for metals (Sparks, 2005). Heavy metals in soils can threaten wildlife health through consumption of contaminated plants. The mean values of the analysed heavy metals in the soil samples showed that Cd level (during the wet season) was higher than the comparable maximum allowable limit. This could have been due to run-offs from farms that had applied fertilizers some distance away from the park.. Raven *et al.* (1998) asserted that the application of certain phosphoric fertilizers inadvertently adds Cd and other potentially toxic elements to soils. It could also be attributed to high level of organic matter as soils high in organic matter adsorb and bind heavy metals by forming complexes with organic acids, which increases the retention of metals in soils. Adetuga *et al*. (2019) also reported high level of cadmium in the soil samples of Old Oyo National Park while Omonona *et al.* (2019) observed low cadmium level in the soil samples of Omo Forest Reserve. Lion and Olowoyo (2013) maintained that Cd enters the environment through the uncontrolled burning of coal and garbage and through the food chain directly or indirectly from plants or animals. The risk of heavy metal poisoning through the food chain increases as the soil concentration rises above the permissible or allowable limits (Baldwin and Marshall, 1999). Consequently, the chronic low-level intake of soil metals through ingestion or inhalation can have a serious negative effect on human and wildlife health (Qu *et al*., 2012; Huang *et al*., 2014). Significant seasonal variation of heavy metal levels was also observed in the sampled soils with wet season having higher concentration of metals (except for Zn, Fe and Pb).

Certain metals and metalloids are essential for plant growth and for animal and human health. With respect to plants, these are referred to as micronutrients and include B, Cu, Fe, Zn, Mn, and Mo (Sparks, 2005). The mean levels of Cu, Ni (wet season), Cr, Fe, Pb, Mn (dry season) and Cd (wet season) were above the comparable WHO permissible limit. These levels are of great concern especially for Pb, Cd and Cr whose toxicity is a great concern (Stankovic *et al*., 2014) and may affect wildlife health. The Cu, Cr and Fe in plant samples is significantly affected by their respective content in soil and others as a result of run-off (Yadav and Khirwar, 2005). Sources of manganese due to human activities in the environment may include combustion of coal, residential combustion of wood, iron and steel production plants and power plants (Calkins, 2009). The application of agricultural inputs such as fertilizers, pesticides, biosolids (sewage sludge), and the disposal of industrial waste and the deposition of atmospheric contaminants increases the total concentration of Cd (Shalini *et al.*, 2017). The bioavailability of Cd in soils determines whether plant Cd uptake occurs to a significant degree (Weggler *et al*., 2004). Cadmium had been reported to induce oxidative stress in plant cells and inactivates some enzymes (Wieczorek *et al*., 2004). Significant seasonal variation of heavy metal levels was also observed in the sampled plant species with wet season having higher concentration of metals (except for Cr, Zn, Mn and Pb).

In conclusion, heavy metals in sampled waterholes (Ni, Cr, Fe, Pb, Mn, Cd), soils (Cd) and plants (Cu, Ni, Cr, Fe, Pb, Mn, Cd) of Okomu National Park were above the comparable permissible limits. This implies that the sampled waterholes may not be safe for drinking. The concentrations of analysed heavy metal and influence of seasonal variation observed in this study has possible implication on wildlife health within the studied ecosystem. As such, there is need to carry out the study (in sediments inclusive) over time so as to monitor heavy metal deposition and route of exposure in the park.

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