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Determination of Heavy Metals in Soil Samples Along the Shores of River Kaduna, Nigeria

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Abstract: Soil samples were collected during dry and wet seasons from 19 sites along the shores of river Kaduna stretching from Kawo in the North to Kudende, an industrial area in the South. The soil samples were analysed for the concentration of seven heavy metals (Cu, Zn, Ni, Fe, Pb, Cd and Mn) using Atomic Absorption Spectrophotometer. The results show that dry season soil contains high level of Fe and Cd with mean values of 718.37±0.01 and 17.59±0.4 mg/kg respectively while wet season soil contains high level of Fe, Cd and Pb with mean values 737.84±0.01, 18.26±0.08 and 410.66±0.09 mg/kg respectively. However, Pb was not detected in the soil samples during the dry season. The mean values obtained from the heavy metals analysed were compared with WHO and EU standard limits and the result shows that the values obtained were above the acceptable range except for Cu values. This study concludes that soil samples along the shores of river Kaduna are polluted and not suitable for agricultural uses. This is attributed to different anthropogenic inputs such as industrial, agricultural, sewage effluent, burning of oil and tyres, plastics, wrapping, dyes, effluent from food, beverage and textile factories that discharges their effluent directly into river Kaduna.

Keywords: Soil, Industrial, Heavy Metals, River Kaduna

1. Introduction

Soil contamination is caused by the presence of man-made chemical or other alterations in the natural soil environment [1]. Elevated concentrations of trace metals as a result of human activities has been recorded in Nigeria. However, excessive releases of wastes into the aquatic environment and the associated health implications only become apparent when anthropogenic contamination of the aquatic environment and its shores was determined [2].

Kaduna metropolis is the administrative headquarters of Old Northern Region and is presently one of the most important cities in Nigeria. Apart from being the administrative headquarters of the state, it experiences high concentration of federal parastatals and many industries including textile factories, automobile plant, refinery, food factories and a number of others. All these industries derive their water requirements from river Kaduna and discharge their wastes ultimately into same, since river Kaduna is the only source of waters for both domestic and Industrial activities. In addition, Kaduna metropolis has experienced increase in population and economic activities, which has led to a steady increase in the quantity, quality and diversity of discharge into the aquatic environment [3]. This increases the concentration of contaminants in river Kaduna above safe limits. Wastes from different sources which are continuously discharged into the river could contribute heavy metals to the river, and alter its water quality alongside soil characteristics [4]. Therefore, pollution of soil and the resulting health effects present some of the biggest challenges affecting the urbanised area of Nigeria such as Kaduna metropolis. Hence this study was aimed at determining the concentration of heavy metals in soil samples along the shores of river Kaduna, Nigeria.

2. Materials and Methods

All the reagents used in this study were of Analar grades and deionized water was used throughout the experimental, except where stated otherwise. All glasswares were washed with detergent and rinsed with water. Further rinsing with

distilled water was carried out before drying in the oven at 103°C. All samples were digested with blanks. Quantisation of metallic content of digested samples and blanks were carried out with computerized Buck 500 model 210VGP Atomic Absorption Spectrophotometer at Kaduna State University (KASU). The samples digested were run on an AAS and metal contents determined from calibration.

2.1. Description of Study Area

Kaduna metropolitan city is located between Latitude 10.9° and 10.15° north of the equator and between Longitude 7.5° and 7.9° east of Greenwich meridian and occupies central portion of Northern Nigeria (Kaduna, 2007). River Kaduna is a tributary of River Niger and is 550 km long, with its source from Kujama hills in Jos, Plateau State and flows 210 km before reaching Kaduna town, where it divides the town into North and South. Beyond Kaduna, the river flows for about 100 km into Shiroro Dam project area past Shiroro, there is another flow length of 200km before it finally discharges into River Niger on the North of Pategi.

2.2. Sampling Points

Nineteen sampling points (Rafinguza, Legislative Quarters, Dalet Barracks, Kawo, Malali Water Board, F. G. C Malali, Angwar Rimi (New Road) Angwar Rimi (New Breeze), Kofar Gamji, Kabala Costain, Kigo Ext, Behind Barnawa Bridge, Behind Kaduna South Water Board, Behind NEPA (PHCN), Down Quarter, Behind UNTL, Behind Lemaco, Behind Flour Mill and Kudende) were selected for soil and water sampling as shown in Figure 1.

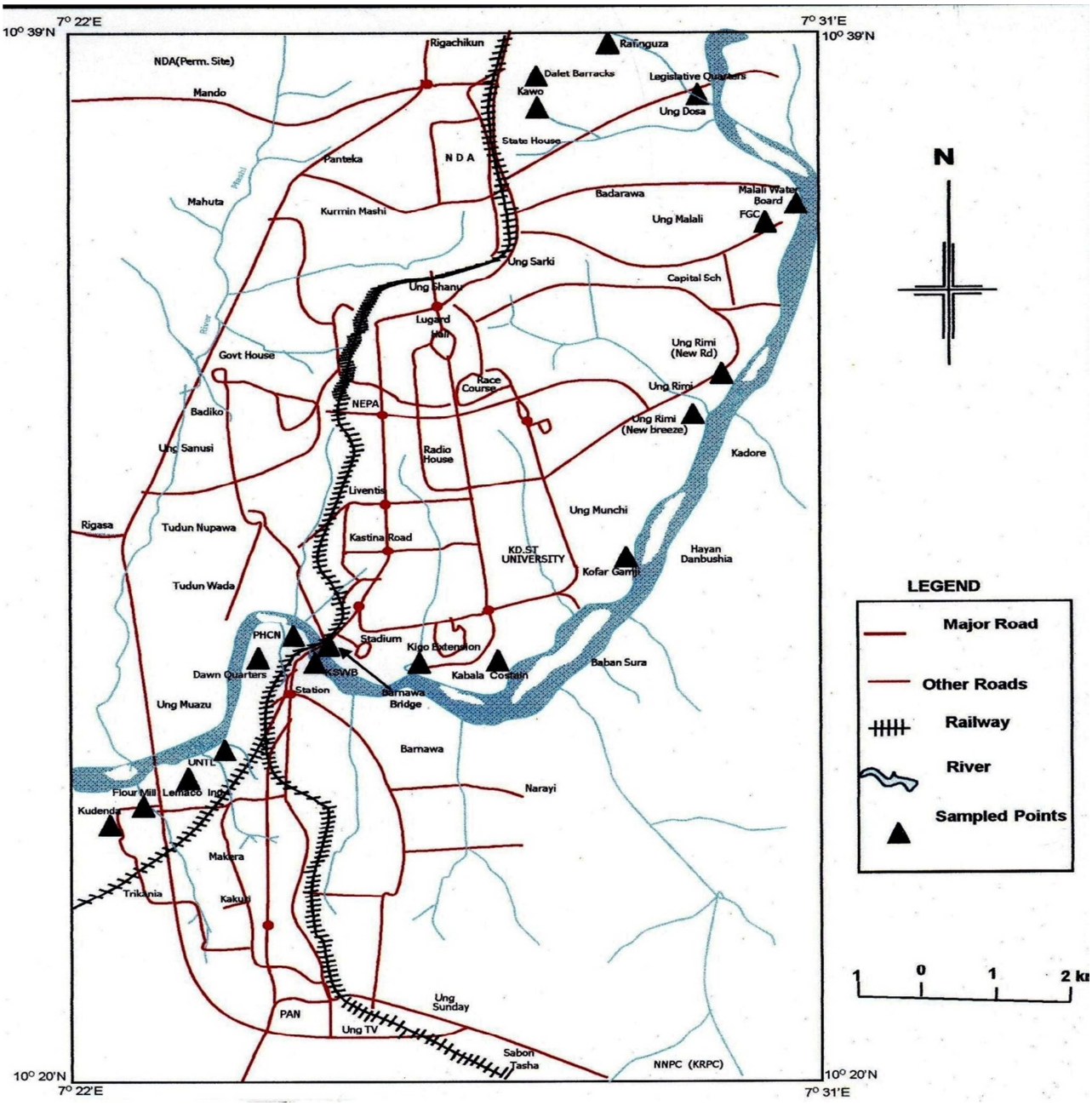

Figure 1. *Map of Study Area.*

2.3. Sample Preparation

Soil samples were also collected from each designated points (Figure 1), all the samples were collected at 0 to 30 cm depth using a soil auger, the samples from the designated points were made into a composite sample. Each composite sample was stored in a tight polythene bag and labelled SD_1-SD_{19} and SW_1-SW_{19} for dry and wet seasons respectively [5].

The samples were oven dried at 105°C, crushed in a porcelain mortar and pestle, sieved through a 2-mm sieve. 1 g of the sieved sample was weighed and transferred into a 100 cm^3 beaker, 5cm^3 of HCl and 15cm^3 and Nitric acid were added to the sample and boiled gently on a hot plate until the volume reduced to about 5cm^3. Deionized water was added and boiled gently again till the volume was approximately 10 cm^3. The suspension was cooled, filtered through a Whatman No. 540 filter paper. The beaker and filter paper were washed with small amount of water until a volume of about 25 cm^3 was obtained. The filtrate was transferred into a 50 cm^3 volumetric flask and was made up to the mark with deionized water and stored in a 100 cm^3 polythene bottles for elemental analysis using Atomic Absorption Spectrophotometer [6].

3. Results and Discussions

Table 1 and 2 shows the results of heavy metal concentration in the soil samples analysed for both dry and wet seasons.

Table 1. *Heavy Metal Concentrations (mg/kg) in soil samples along shores of River Kaduna during Dry Season (SD).*

ID	Cu	Zn	Ni	Fe	Pb	Cd	Mn
SD_1	17.50±0.06	154.0 ± 0.01	ND	840.00±0	ND	ND	ND
SD_2	13.00±0.06	231.± 0.01	67.00±0.58	778.00±0.02	ND	ND	113.00±0.04
SD_3	7.00±0.06	154.0 ± 0.00	ND	831.00±0.02	ND	ND	192.00±0.04
SD_4	ND	20.50± 0.01	84.00±0.58	ND	ND	21.50±0.02	ND
SD_5	9.50±0.00	151±0.01	134.00±0.58	853.00±0.02	ND	ND	ND
SD_6	8.00±0.06	285 ± 0.01	100±0.00	ND	ND	21.50±0.04	67.00±0.00
SD_7	8.00±0.06	164.50±0.01	184.00±0.58	773.00±0.02	ND	ND	ND
SD_8	13.00±0.06	207.50±0.01	184.00±0.58	806.00±0.00	ND	50.70±0.25	113.00±0.04
SD_9	17.50±0.06	198.00±0.01	234.00±0.58	964.00±0.02	ND	29.00±0.25	181.00±0.04
SD_{10}	11.80±0.06	213.50±0.00	134.00±0.58	869.00±0.00	ND	ND	11±0.00
SD_{11}	11.00±0.07	35.50±0.01	267.00±0.58	644.00±0.02	ND	101.00±0.25	ND
SD_{12}	21.00±0.06	275.50±0.00	317.00±0.58	934.00±0.00	ND	22.00±0.01	156.00±0.00
SD_{13}	13.00±0.06	233.50±0.01	267.00±0.58	800.00±0.02	ND	22.00±0.02	315.00±0.00
SD_{14}	13.00±0.06	217.50±0.01	250.00±0.00	938.00±0.02	ND	ND	ND
SD_{15}	8.00±0.06	56.50±0.01	200.00±0.00	791.00±0.00	ND	44.00±1.36	315.00±0.00
SD_{16}	27.00±0.06	187.50±0.06	134.00±0.58	ND	ND	ND	315.00±0.00
SD_{17}	17.50±0.06	265.00±0.01	184.00±0.58	996.00±0.00	ND	ND	229.00±0.00
SD_{18}	8.00±0.06	151.00±0.01	134.00±0.58	876.00±0.00	ND	ND	73.00±0.00
SD_{19}	14.50±0.00	250.00±0.00	ND	956.00±0.00	ND	22.00±0.02	365.00±0.00
Mean	12.54±0.05	181.79±0.01	151.26±0.40	718.37±0.01	ND	17.59±0.04	150.00±0.01

Table 2. *Heavy Metal Concentrations (mg/kg) in soil samples along shores of River Kaduna during Wet Season (SW).*

ID	Cu	Zn	Ni	Fe	Pb	Cd	Mn
SW_1	8.00±0.06	77.00±0.01	84.00±0.58	992.00±0.17	1000.00±0.00	29.±0.25	ND
SW_2	45.0±0.00	227.0±0.01	84.00±0.58	801.00±0.02	400.00±0.00	51.±0.25	131.±0.4
SW_3	6.50±0.06	23.00±0.01	336.00±0.58	797.00±0.00	1150.00±0.00	72±0.25	131±0.4
SW_4	ND	17.00±0.01	84.00±0.58	ND	300.00±0.00	ND	ND
SW_5	8.00±0.06	61.00±0.01	15.00±0.00	1000.00±0.00	ND	ND	484±0.04
SW_6	6.50±0.06	45.00±0	336.00±0.58	985.00±0.02	700.00±0.00	ND	293.±0.0
SW_7	45.0±0.00	16.00.±0.01	84.00±0.58	689.00±0.00	400.00±0.00	22.±0.00	ND
SW_8	6.50±0.06	78.00±0.01	134.00±0.58	773.00.±0.02	250.00±0.00	ND	403.±0.4
SW_9	45.00±0.00	39.00±0.01	134.00±0.58	931.00±0.02	50.00±0.00	72.00±0.25	235.00±0.04
SW_{10}	ND	ND	134.00±0.58	15.00±0.00	ND	ND	ND
SW_{11}	11.0±0.06	44.00±0.00	84.00±0.58	842.00±0.00	200.00±0.00	29.00±0.25	235.±0.04
SW_{12}	10.00±0.00	65.00±0.00	65.00±0.58	434.00±0.00	200.00±0.00	22.00±0.00	ND
SW_{13}	8.00±0.00	40.00±0.01	234.00±0.58	934.00±0.02	550.00±0.01	ND	ND
SW_{14}	ND	229.0±0.01	234.00±0.58	980.00±0.02	534.00±0.58	ND	ND
SW_{15}	ND	26.00±0.01	134.00±0.58	50.00±0.00	51.00±0.00	50±0.25	1975.±0
SW_{16}	24.0±0.00	206.±0.01	336.00±0.58	937.00±0.00	634.00±0.58	ND	163.00±0.04
SW_{17}	27.0±0.06	327.0±0.01	284.00±0.58	993.00±0.00	1050.00±0.00	ND	336.±0.0
SW_{18}	8.00±0.06	26.0±0.01	238±0.58	894±0.00	200±0.00	ND	78±0.04
SW_{19}	15.00±0.0	8.00±0.01	233.00±0.58	972.00±0.00	133.50±0.58	ND	375.±0.0
Mean	15.50±0.03	81.79±0.01	177.21±0.13	737.84±0.01	410.66±0.09	18.26±0.08	254.68±1.50

The mean heavy metal concentrations in soil samples along the shores of river Kaduna shows that Cu contents ranged from ND - 27.00 mg/kg during dry seasons while during the wet seasons Cu values ranged from ND to 45.00 mg/kg. The concentration of Cu in soil samples obtained in this study was higher than 0.19 mg/kg of copper in soil reported from background uncontaminated soil by Adeniyi and Afolabi and 2.8 - 18.9 mg/kg in a similar study by Fatoki, but lower than the standard limits set by EU [7-9]. Copper is usually presents in soils within the range of 0 - 250 mg/kg [10]. In this study, the copper with highest value at 27.00mg/kg was obtained in samples SD_{16} and SW_{17} as a result of industrial wastes from factories sited along river Kaduna.

Zn contents in the soil samples ranged from 20.50 – 285.00 mg/kg during dry seasons while during wet seasons, it ranged from ND to 327.00 mg/kg. The range of Zinc concentrations in this study was higher than the reported value of 4.75 - 16.16 mg/kg in uncontaminated soil samples in other locations as reported by Alexander and Pasquini and 0.60 - 4.95 mg/kg reported in a similar study by Fatoki [8, 11]. In this study, the highest concentration for Zn with 327.00 mg/kg was in line with similar study reported by Akbar *et al*., with values ranging from 467- 480 mg/kg [12].

Ni contents in the soil samples ranged from ND – 317.00 mg/kg during dry season while in wet season values ranging from 15.00 mg/kg to 336.00 mg/kg was obtained. Concentration of Ni in the soil samples were much higher than 0.99 and 1.20mg/kg reported by Audu and Lawal and 1.20 mg/kg reported by John and Stephen. Although values obtained in this study were high compared to the World average of 20 mg/kg [13-15]. In this study, the least value of 15.00 mg/kg was obtained in sample SW_5 while the highest value of 336.00 mg/kg was obtained in samples SW_3, SW_6 and SW_{16} which implies that industrial and agricultural effluents could be responsible for high levels of Ni from these sites. However high level of Ni in this study could be due to discharge of industrial and agricultural wastes into the river. Fe contents in the soil samples ranged from ND to 996.00 mg/kg during the dry season while during the wet seasons values ranging from ND to 1000.00 mg/kg was obtained. The concentration of Fe in the soil samples is much higher than values from background uncontaminated soil (0.19 mg/kg) by Anthony and Balwant, and values of 2.8 - 18.9 mg/kg in a similar study by Audu and Lawal [13, 16]. In this study, the highest value of 1000.00 mg/kg was obtained in sample SW_6, which implies that domestic effluents could be responsible for high levels of Fe from this site. Pb contents was not detected in soil samples during dry seasons, while values ranging from ND to 1150.00 mg/kg was obtained during wet season. Cd contents in soil ranged from ND to 101.00 mg/kg during the dry season while it ranged from ND to 72.00 mg/kg during wet seasons. Mn contents in the soil samples ranged from ND to 365.00 mg/kg during dry season while in wet season it ranged from ND to 1975.00 mg/kg. The highest level of Mn (365.00 mg/kg) obtained in sample SD_{19} in this study was higher than the range of 170 - 258.5 mg/kg and lower than 408.00 mg/kg reported by Ansari *et al.*, and by Ho and Tai respectively [17-18]. The Mn content in the soils were above the limits of the critical soil concentration, implying contamination due to industrial activities within the area [9, 19].

Using one-way analysis of variance (ANOVA), the heavy metal concentration in soil samples along the shores of river Kaduna for dry and wet seasons revealed statistically significant differences in Zn, Cu and Pb at ($P < 0.01$). However, no significant difference was observed between Ni, Fe, Cd and Mn. Furthermore, Positive correlations were observed between Cu and Zn, Zn and Mn, Ni and Cd, Ni and Pb, Ni and Fe at ($p < 0.05$) and ($P < 0.10$).

4. Conclusion

From the results obtained, this study concludes that soil samples along the shores of river Kaduna are polluted and not suitable for agricultural uses. This could be attributed to different anthropogenic inputs such as industrial, agricultural, sewage effluent, burning of oil and tyres, plastics, wrapping, dyes, effluent from food, beverage and textile factories that discharges their effluent directly into the river. The concentration of some of the heavy metals present were above the WHO and EU recommended safe limits, therefore the industries located along the river should be advised to treat their effluent before discharging into the river. It is recommended that the enforcement of public health laws and regularities of the area should be given the urgent attention it deserves, law enacted by Federal Government and Kaduna State Government to protect the environment should be enforced to reduce the deposition of wastes. Follow-up studies to monitor the bioaccumulation of contaminants are recommended in order to evaluate the health risks.

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