Original Research Article

Assessment of Selected Heavy Metals in Sediments from Ndambuk River, Busia County, Kenya

Abstract

Anthropogenic activities have significantly contributed to soil and sediment pollution. Heavy metals are among the most common soil/sediment pollutants, owing to the fact that they easily get adsorbed on sediment surfaces and get carried from one ecosystem to another. This study examines the pollution effect of heavy metals in sediments from River Ndambuk, Busia County, Kenya. A total of eight heavy metals (Co, Cu, Fe, Cr, Ni, Cd, Pb and Zn) were examined during dry and wet seasons. The levels of Cd, Ni and Pb were above the WHO permissible limits. However, Pb levels were only above the WHO limit during the dry season, with the wet season registering concentrations way below WHO limits. Co, Cu, Fe, Cr and Zn recorded concentrations below WHO limits during the dry and wet seasons. Pollution indices were used to determine the extent of sediment pollution. Geoaccumulation index, pollution load index, contamination factor and enrichment factor were calculated from the heavy metal concentrations in sediments. Fe, Cr and Zn recorded negative I geo values during both seasons, signifying no pollution by these metals. Ni recorded moderately polluted to strongly polluted status whereas Pb recorded strongly polluted status only during the dry season. Points 1 - 4 recorded lack of pollution due to anthropogenic activities, while points 5 - 7 recorded pollution due to anthropogenic activities as per the PLI values. The study recommends proper land use and dumping of wastes and controlled mining activities to keep soil pollution at bay.

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1.0 INTRODUCTION

The quest to achieve rapid economic development by African countries has led to industrialization and urbanization, leading to the pollution of water bodies such as lakes and rivers, especially those located in urban and industrialized areas. Heavy metals are one of the leading causes of water polluting, affecting both aquatic and terrestrial life forms, leading to the

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destruction of plants, biodiversity as well as ecological structures (Yang et al., 2020). Heavy metals are related with a number of health complications in humans. Suspended particles in water usually have a significant amount of heavy metals adsorbed on their surfaces, leading to a rise in the levels of these metals in water. The study of heavy metals in suspended particles and sediments can aid in the evaluation of health related risks, evaluate the extent to which a water source has been polluted, trace the origin of pollutants and develop strategies to mitigate water pollution (Zhang et al., 2023). In as much as the levels of heavy metals in sediments can provide crucial information about the pollution status of a particular water body, much still needs to be done to as this is not enough to evaluate the effects of anthropogenic activities on polluted sediments since the level of metals in sediments will mainly depend on two main factors: the chemical forms of the heavy metals and the rate at which the metals bind on sediment particles (Yangguang et al., 2012). The concentration of heavy metals in soil and sediments also depends upon several factors such as the soil temperature, pH, organic matter content and salinity. These factors greatly influence the rate at which heavy metals remain bound in soil/sediment particles and as a result dictate the migration of these cations from one place to another. When animals feed on food that is contaminated with heavy metals, it leads to the bioaccumulation of the said metals in the organism's tissues and this can be passed up the food chain. (Liu et al., 2019). Different heavy metals pose different health risks in humans. Bioaccumulation of lead in the human body leads to asthma in adults, neurological disorders in children as well as complicated pregnancies in women of child bearing age. Bioaccumulation of chromium and nickel leads to inflammation of the body as well as chronic respiratory conditions such as asthma. High levels of cadmium in the body may result in osteoporosis and hypertension, as well as kidney damage. Arsenic is regarded as one of the most poisonous heavy metals globally and its bioaccumulation may result in heart disease while chronic exposure to arsenic may result in type II diabetes. Manganese affects the central nervous system, leading to neuron coordination problems. Some heavy metals are well known carcinogens as they bioaccumulation is associated with liver, lung and kidney cancer (Shahir et al., 2021). Due to the dangers posed by the high levels of heavy metals in soil, there is need to develop mechanisms that are capable of getting rid of heavy metals in soil. A number of techniques can be employed in the process of soil remediation. They include physical methods such as the replacement of contaminated soil as well as thermal treatment of soil; chemical methods such as soil washing and stabilization and biological methods such as the use of microorganisms to get rid of heavy metals from soil. Of all the above methods, soil washing is the most effective since it is much simpler than the other remediation techniques and is also capable of completely getting rid of heavy metals from soil. Chemical remediation method involves the use of various reagents, among them chelating agents as well as acids and bases (Jiyan et al., 2020).

2.0 MATERIALS AND METHODS 2.1 Study Area

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The location of Busia County is 0° 29' 45" N and 34° 7' 59" E (Mindat, 2023). According to the 2019 population census, the County had a population of 893,681 people, with a population density of 526.8 km². The climate of the County is tropical rainforest with temperatures ranging from 16 - 31 °C with two seasons namely dry and wet. Dry season covers the period between January and March with the highest recorded temperatures being 31 °C. The wet season on the other hand covers the period between April and September with average temperatures of about 27 °C (Busia climate, 2023). The origin of river Ndambuk is Samia hills from where it flows through the highly populated areas of Busia town such as Korinda, Amerkwai, before passing through sub counties such as Alupe and Adungosi where sugarcane, maize and millet farming is heavily practised, before crossing into neighbouring Uganda into Okame. Otakwa and Omanye areas. The first section of the river, upstream, mainly comprises of urban centres in which small scale industries, garages and shops are located. The second section is heavily agricultural and mainly comprises of sugarcane, maize, millet and sorghum plantations. The third section, downstream, mainly comprises of gold mines where both large scale and artisan gold mining is heavily practised, especially in neighbouring Uganda where mining activities are poorly regulated. These anthropogenic practices contribute to the discharge of heavy metals into the river, leading to pollution of the river. The portion of the river under study is from Amerikwai area in Busia town to Omanye across the Kenya - Uganda border. Figure 1 below presents the study area and the sampling points.

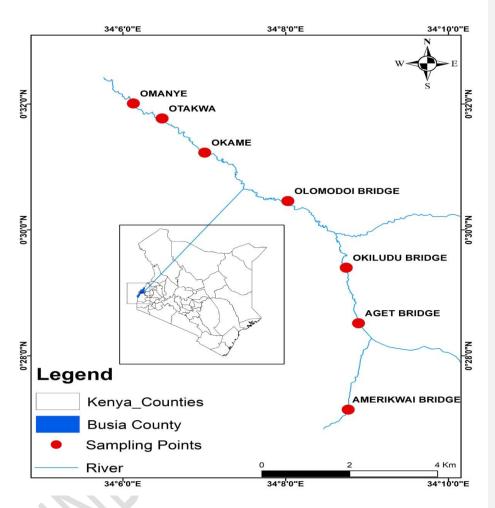


Figure 1: Map of River Ndambuk with sampling points (Source: Authors)

Table 1: Sampling Points and Descriptions along River Ndambuk

Station Code	GPS Coordinates	Description
S1	[0.4473178 N; 34.14581 E]	Amerikwai bridge in Busia town
S2	[0.475463 N; 34.148456 E]	Aget bridge
S3	[0.489743 N; 34.145468 E]	Okiludu bridge
S4	[0.507436 N; 34.133754 E]	Olomodoi bridge
S5	[0.52013 N; 34.1166880 E]	Okame
S6	[0.5292540 N;34.107975 E]	Otakwa
S7	[0.533175 N; 34.102220 E]	Omanye

2.2 Sampling and Analytical Procedures

Sediment sampling was carried out during both the dry and wet seasons (January 2023 and April 2023 respectively). Random sampling was done in order to eliminate sampling bias. Consistency in the sampling process was guaranteed using the Global Positioning System (GPS). Sampling coordinates were taken during the dry season sampling process to ensure that the sediment samples were collected at the exact same spot during the wet season so as to eliminate sampling error (Ondoo *et al.*, 2019). Seven sediment samples were collected from a depth of 0 to 15 cm in all the seven sampling points during both the dry and wet seasons. A total of five sub samples were collected at each sampling point using an auger made from stainless steel. Parts of the sample with direct contact to the auger were discarded to minimize contamination. The composite samples were placed in polyethylene (PVC) bags to prevent oxidation and further changes to chemical composition; after which they were transported to the Alupe university chemistry laboratory for further processing (Shahla *et al.*, 2021).

The sediment samples were then dried in an oven at 105 °C after which particle size reduction was carried out by crushing and grinding. The ground sample was then passed through a sieve to obtain sediment particles of uniform size. This was then followed by coning and quartering, where the sample was piled into a cone, the top flattened then the sample divided into four equal portions and the two opposite portions discarded. The remaining portions were continuously taken through the coning and quartering process until a representative sample was obtained (Harvey, 2000).

2.2.1 Heavy Metal Analysis of Sediments

Acid digestion was employed to bring the sediment samples into solution form for analysis by Flame Atomic Absorption Spectroscopy (FAAS). In a 250 mL conical flask, 1g of sediment was placed for digestion. 10 mL of 50% HNO₃ was added to the sample and the mixture heated on a hot plate at 95 °C. Care was taken to ensure boiling did not take place. This was followed by refluxing with 65% HNO₃ until brown fumes of NO₂ were no longer produced. Further heating was carried out until the total volume of the mixture reduced to 5 mL. This was followed by the addition of 10 mL of 30% H₂O₂ after cooling, followed by refluxing with 10 mL of 37% HCl at a

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temperature of 95 °C for a period of 15 minutes. The final step was filtration of the digestate using Whatman No. 42 filter paper. The samples were filled up to the 100 mL mark of a volumetric flask using distilled water (EPA, 1989).

2.3 Statistical Analysis

The Statistical Package for Social Sciences (SPSS) was used to analyse the data obtained. The concentration of each heavy metal was measured in triplicate and the data obtained reported as mean \pm standard deviation to demonstrate precision of the obtained data. Seasonal variations of the heavy metals were determined using paired t – test at 95% level of confidence (P < 0.05). Spatial variations for both the dry and wet seasons were determined using One way Analysis of variance (ANOVA) which is a statistical method for comparing three or more data sets, at 95% level of confidence (P < 0.05) (James and Jane; 2010).

2.4 Pollution Indices

To determine the extent to which the sediments had been contaminated by heavy metals, pollution indices such as enrichment factor, pollution load index, contamination factor as well as geoaccumulation index were determined (Nowrouzi and Alireza, 2014). Background values used in the determination of both enrichment factor and geoaccumulation index were adopted from Taylor and Mc Lennan, 1995 (Taylor and Mc Lennan, 1995).

2.4.1 Geoaccumulation Index

Sediment pollution and environmental effect of pollution by heavy metals can be determined by geoaccumulation index (I_{geo}). Originally defined by Muller, I_{geo} determines the extent to which sediments are polluted by heavy metals by drawing comparisons between present heavy metal concentrations with the concentrations in preindustrial era (Nowrouzi, 2014). Geoaccumulation index can be calculated using the formula below:

$$I_{geo} = log_2 \frac{C_i}{1.5C_b}$$

Where:

 C_i = concentration of the metal under investigation in sediments

C_b = geochemical background of the metal under investigation in sediments

1.5 = a value factored into the equation to account for environmental differences in background values (Cardellicchio *et.al.*, 2010).

Muller (1981) presented seven classes of geoaccumulation index as shown in the table below:

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Table 2: Classes of Geo – accumulation index (Muller 1981)

I _{geo} Value	Class	Sediment Quality
<u>≤ 0</u>	0	Unpolluted
0 - 1	1	Unpolluted - moderately polluted
1 to 2	2	Moderately polluted
2 to 3	3	Moderately – strongly polluted
3 to 4	4	Strongly polluted
4 to 5	5	Strongly polluted - extremely polluted
> 5	6	Extremely polluted

2.4.2 Contamination Factor

Used to determine the extent to which sediment is contaminated in a given location, the contamination factor is determined as per the equation below:

$$C_f^i = \frac{c_{o-n}^i}{c_b^i}$$

Where:

 $C_0^i - n$ = average concentration of the element of interest in sediments

 C_b^i = refers to the background concentration of the element of interest (Dimuthu, 2016).

The contamination factor classes for sediment quality are presented in the table below:

Table 3: Contamination factor classes for sediment quality

Contamination Factor Value	Sediment Quality
≤1	Low contamination
1 - 3	Moderate contamination
3 – 6	Considerable contamination
> 6	Very high contamination

2.4.3 Enrichment Factor

The enrichment factor in sediments is calculated as:

$$\frac{\binom{C_x}{C_{Fe}}_{sample}}{\binom{C_x}{C_{Fe}}_{background}}$$

Where:

(C_x/C_{Fe}) sample = concentration of the metal of interest and iron in the sediment sample

 $(C_x \text{ and } C_{Fe})$ background = concentration of the metal of interest and iron in the background respectively

Enrichment factor values are indicative of sediment quality as presented in the table below:

Table 4: Enrichment factor classes for sediment quality

Enrichment Factor Value	Sediment Quality
< 1	No enrichment
1 - 3	Minor enrichment
3 - 5	Moderate enrichment
5 - 10	Moderately severe enrichment
10 - 25	Severe enrichment
25 - 50	Very serious enrichment
> 50	Extremely severe enrichment

2.4.4 Pollution Load Index

In determining the level of pollution in sediments, pollution load index is used.

Pollution load index is determined by the formular:

$$PLI = (C_{f1} \times C_{f2} \times \times C_{fn})^{\frac{1}{n}}$$

Where:

 C_{f1} , C_{f2} and C_{fn} = contamination factor for the first, second and n^{th} element respectively

n = total number of elements under study (Dimuthu, 2016).

PLI > 1 = Pollution from anthropogenic activities

PLI < 1 = No pollution from anthropogenic activities

3.0 RESULTS AND DISCUSSION

3.1 Cadmium

The concentration of Cadmium in sediments ranged from 1.13±0.06 – 18.13±0.45 mg/kg during the dry season to $1.44\pm0.08 - 19.52\pm0.44$ mg/kg during the wet season. Paired t – test revealed no significant difference between the dry and wet seasons, with T calculated = 0.79 < T critical = 2.45 at P < 0.05 confidence level. Spatial variations were statistically significant as per one – way ANOVA, with F calculated = 1848.02 and 1097.08 for dry and wet seasons respectively, > F critical = 2.85 at P < 0.05 confidence level. The high Cadmium levels at sampling points 1, 3 and 4 during the dry season can be linked to evaporation of water from the river leading to an increase in concentration of the analyte However, high levels of Cadmium at sampling points 2, 5, 6 and 7 during the wet season can be linked to surface runoff carrying Cadmium rich pollutants into the river. All the sampling points recorded Cadmium concentrations above the WHO limit of 3.0 mg/kg; except sampling points 5 and 6 (during the dry season) and sampling point 4 (during the wet season). These high Cadmium levels in sediments are as a result of discharge of untreated sewer into the river, dumping of batteries and other Cadmium rich pollutants into the river and the use of Cadmium rich pesticides in farming and the discharge of untreated waste water from the numerous gold mining and metal processing sites located downstream. This explains high Cadmium pollution during the wet season. The level of Cadmium reported in this study was way above that reported by Sayo et al., during the determination of heavy metals in soil and vegetables irrigated with sewage effluent: a case study of Embu sewage treatment plant, Kenya (Sayo et al., 2020).

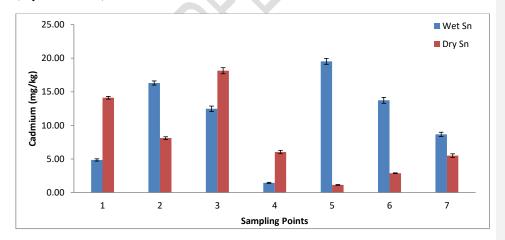


Figure 2: Cadmium levels in sediments during the dry and wet seasons

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3.2 Cobalt

Cobalt finds wide spread use in the paint industry, especially in the manufacture of pigments and driers. Cobalt levels in river Ndambuk ranged from 14.62±0.25 - 59.27±0.43 mg/kg during the dry season, to $2.10\pm0.09 - 38.03\pm0.39$ mg/kg during the wet season. There was no significant difference in seasonal variations, with T calculated = $2.12 < T_{critical} = 2.45$ at P < 0.05 confidence level. However, spatial variations were statistically significant with F calculated = 5307.73 and 4490.21 during the dry and wet seasons respectively, > F critical = 2.85 at P < 0.05 confidence level. Only sampling points 2 and 7 recorded cobalt levels above the WHO recommended levels of 50 mg/kg during the dry season, whereas all the sampling points recorded Cobalt levels below the WHO limit of 50 mg/kg during the wet season. The high levels of Cobalt at sampling point 2 during the dry season can be attributed to the tributaries joining the main river at this point, leading to the discharge of Cobalt rich pollutants from other parts of the sub catchment. The high level of Cobalt at sampling point 7 during the dry season can be attributed to increased anthropogenic activities downstream, particularly mining activities as well as metal processing factory located downstream. The Cobalt levels below the WHO limits in all the sampling points during the wet season can be linked to dilution by rain water, leading to decreased analyte concentration. Cobalt concentrations reported in this study were within the range of those reported by Olaka et al., in the study of heavy metals in surface sediments of Lake Naivasha in Kenya (Olaka et al., 2020).

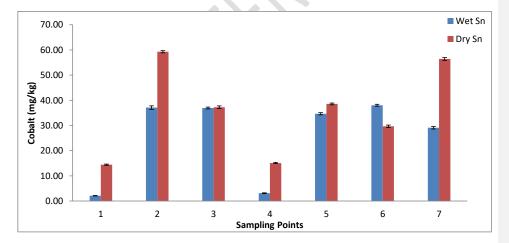


Figure 3: Cobalt levels in sediments during the dry and wet seasons

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3.3 Copper

Copper levels recorded in this study ranged from $4.15\pm0.28-44.02\pm0.36$ mg/kg during the dry season to 22.72±1.54 - 137.24±12.16 mg/kg during the wet season. There was a significant difference in seasonal variations with T calculated = 3.23 > T critical = 2.45 at P < 0.05 confidence level. Spatial variations followed the same trend, with F calculated = 2692.12 and 194.14 for the dry and wet seasons respectively. This was greater than F $_{critical} = 2.85$ at P < 0.05 level of confidence. All the sampling points recorded Copper levels below the recommended WHO limit of 100 mg/kg during both the dry and wet seasons, except sampling point 7 whose concentration was 137.24±12.16 mg/kg. This can be attributed to increased mining activities downstream, where untreated effluent is discharged into the river. The metal processing factory located downstream only serves to worsen pollution by heavy metals. During the wet season, copper levels in all the sampling sites were higher than the concentrations during the dry season. This, coupled with the steady increase in Copper levels downstream can be attributed to increased anthropogenic activities downstream. These include: discharge of untreated sewer from the densely populated Busia town, use of Copper based pesticides and herbicides in farming unregulated mining activities and metal processing factory located downstream. The levels of Copper recorded in this study were above the levels obtained by Yan et al., in the assessment of ecological risks and probable sources of Cu, Zn and Mn in river Tana sediments in Kenya (Yan et al., 2022).

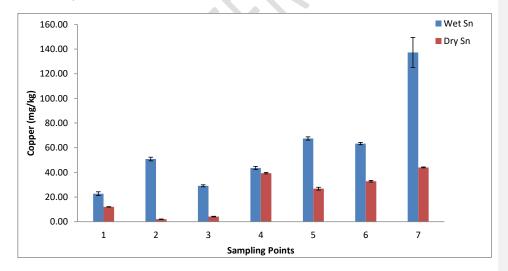


Figure 4: Copper levels in sediments during the dry and wet seasons

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3.4 Iron

Iron finds wide application in the manufacture of different products, ranging from pigments in paints to stainless steel. Iron levels during the dry season were $13021.60\pm141.51-21080.01\pm184.74$ mg/kg during the dry season and $13384.49\pm174.55-22057.25\pm144.94$ mg/kg during the wet season. There was no significant difference in seasonal variation with T calculated = 0.07 < T critical = 2.45 at P < 0.05 level of confidence. Spatial variations were however significantly different at P < 0.05 level of significance, with F calculated = 480.44 and 972.37 during the dry and wet seasons respectively, > F critical = 2.85. All the sampling points recorded iron levels way below the WHO recommended levels of 50,000 mg/kg during both seasons, indicating no pollution from iron. The levels of iron obtained in this study were much higher than those obtained by Ondoo *et al.*, during the assessment of heavy metals in sediments from river Sio, in Busia County, Kenya (Ondoo *et al.*, 2019).

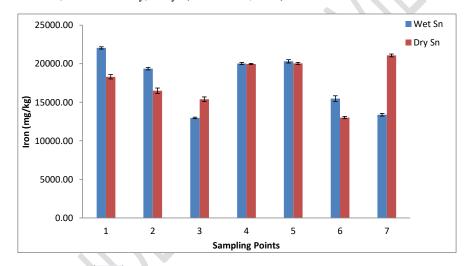


Figure 5: Iron levels in sediments during the dry and wet seasons

3.5 Chromium

The application of Chromium in paint, automobile and pesticide industry makes the metal one of the leading heavy metal pollutants. Chromium registered a concentration of $2.73\pm0.15-8.40\pm0.10$ mg/kg during the dry season, to $0.5\pm0.006-9.63\pm0.25$ mg/kg during the wet season. There was no significant difference in seasonal variation, with T calculated = 2.36 < T critical = 2.45 at P < 0.05 level of confidence. Spatial variations were however statistically significant with F calculated = 628.63 and 851.25 during the dry and wet seasons respectively, against T critical = 2.85 at P < 0.05 confidence level. All the sampling points registered Chromium levels way below the WHO recommended levels of 100 mg/kg during both the dry and wet seasons, indicating no

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pollution from chromium. The high Chromium levels recorded during the dry season can be linked to water evaporation from the river leading to increased analyte concentration, but this is offset during the wet season by dilution, resulting in a decrease in the concentration of Chromium. Sampling point 2 reported the highest level of Chromium during the dry season (8.40±0.10 mg/kg) and this is attributed to the tributaries joining the river at this point, bringing in Chromium rich pollutants from other parts of the catchment. Sampling point 5 recorded the highest concentration of chromium during the wet season (9.63±0.25 mg/kg) and this is mainly due to the gold mines and metal processing factory located downstream as they discharge untreated waste water into the river leading to elevated chromium levels. The steady rise in the levels of chromium downstream during both the dry and wet seasons can be attributed to increased anthropogenic activities such as farming, mining and manufacturing (metal processing factory) which discharge waste into the river leading to increased levels of Chromium. Chromium levels obtained in this study are much lower than those obtained by Jirsa *et al.*, in the distribution of heavy metals and other trace elements in water, sediments and macrophytes in Kenyan parts of Lake Victoria (Jirsa *et al.*, 2019).

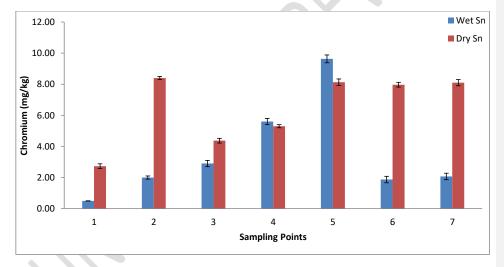


Figure 6: Chromium levels in sediments during the dry and wet seasons

3.6 Lead

Lead finds wide application in pesticides, in fuels as an antiknock additive (tetraethyl lead) and in the pigment industry. Lead levels in river Ndambuk ranged from $227.09\pm5.95-515.65\pm7.01$ mg/kg during the dry season to $7.86\pm0.59-18.32\pm0.66$ mg/kg during the wet season. Paired t – test revealed significant difference in seasonal variations with T _{calculated} = 10.23 > T _{critical} = 2.45 at P < 0.05 confidence level. A similar trend was reported for spatial variations with F _{calculated} = 175.25 and 144.04 for dry and wet seasons respectively against F _{critical} = 2.85 at P < 0.05

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confidence level. All the seven sampling points reported Lead levels way above the WHO limit of 100 mg/kg during the dry season. The trend was however reversed during the wet season, with all the sampling points recording levels of Lead way below the WHO recommended limit. The low levels of Lead during the wet season can be attributed to dilution by rain water leading to a significant decrease in the concentration of the metal. The high levels of Lead during the dry season can be attributed to the discharge of untreated sewer into the river, the use of Lead rich pesticides and herbicides in agriculture as well as the dumping of solid waste consisting of paint products and used batteries into the river. Lead levels reported during the wet season in this study were in line with those reported by Zaharin *et al.*, in the application of geoaccumulation index and enrichment factors in assessment of heavy metal pollution in sediments (Zaharin *et al.*, 2013).

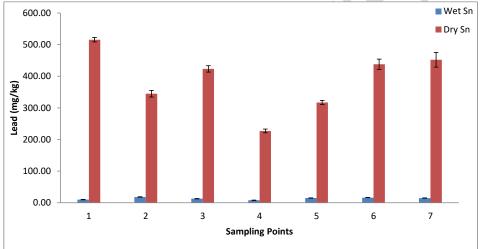


Figure 7: Lead levels in sediments during the dry and wet seasons

3.7 Nickel

Nickel is crucial in the manufacture of coins, industrial machine parts such as heat exchangers as well as stainless steel. The levels of Nickel recorded in river Ndambuk was $174.58\pm3.67-262.03\pm4.45$ mg/kg during the dry season to $75.87\pm1.01-132.01\pm1.32$ during the wet season. Seasonal variations were significantly different at P < 0.05 level of significance, with T calculated = 5.84, > T critical = 2.45. Spatial variations were also statistically significant at P < 0.05 with F calculated = 277.06 and 635.96 during the dry and wet seasons respectively, > F critical = 2.85. The concentration of Nickel was high in all the sampling points during the dry season, which can be attributed to evaporation of water from the river leading to increased analyte concentration. However, this effect is offset during the wet season due to dilution by rain water leading to a decreased analyte concentration. Sampling point 2 recorded the highest concentration of Nickel

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during the dry season, which can be linked to the smaller tributaries that join the main river at this point hence bringing in Nickel – rich pollutants from all other parts of the sub catchment. All the sampling points registered Nickel levels way above the WHO permissible limits of 50 mg/kg during both the dry and wet seasons, indicative of pollution by Nickel. These high Nickel levels are from raw sewage as Busia town has poor sewerage infrastructure, waste water from mines and metal processing factories as well as surface runoff from garages and workshops located close to the river. The increase in Nickel levels downstream during the wet season is indicative of increased anthropogenic activities downstream. The levels of Nickel obtained from river Ndambuk are way higher than those recorded by Kinuthia *et al.*, in the analysis of heavy metals in waste water and soil samples in open drainage channels in Nairobi, Kenya (Kinuthia *et al.*, 2020).

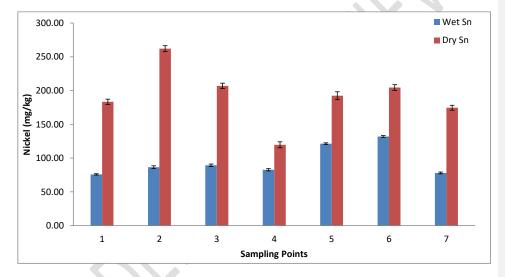


Figure 8: Nickel levels in sediments during the dry and wet seasons

3.8 Zinc

The application of Zinc and Zinc related compounds in the manufacture of pigments, paints, wood preservatives and inorganic fertilizers has led to increased pollution by Zinc in the environment. The recorded levels of Zinc from sediments in the Ndambuk river ranged from $13.52\pm1.13-56.40\pm2.13$ mg/kg during the dry season to $30.70\pm1.52-54.17\pm1.75$ mg/kg during the wet season. Seasonal variations were not significantly different at P < 0.05 level of significance, given that T calculated = 2.35 < T critical = 2.45. However, spatial variations were statistically significant at P < 0.05 confidence level, with F calculated = 27.35 and 139.24 during both the dry and wet seasons respectively, P > T critical = 2.85. All the sampling points registered Zinc levels way below the WHO limit of 300 mg/kg during both the dry and wet seasons,

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therefore indicating no pollution by Zinc. Zinc levels below the WHO limit of 300 mg/kg were also reported by Ondoo et al., during the determination of heavy metals in sediments in river Sio, Busia County, Kenya (Ondoo *et al.*, 2019)

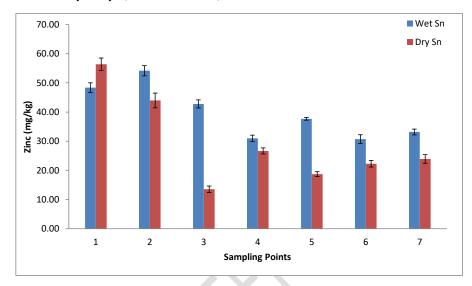


Figure 9: Zinc levels in sediments during the dry and wet seasons

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Table 5: Heavy metal concentration in sediments during the dry and wet seasons

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Parameter (mg/kg)	Season	S1	S2	S3	S4	S5	S6	S7	WHO Limit
a	Dry	14.10±0.20	8.10±0.20	18.13±0.45	6.03±0.25	1.13±0.06	2.87±0.06	5.50±0.26	3
Cadmium	Wet	4.85±0.17	16.30±0.31	12.46±0.41	1.44±0.08	19.52±0.44	13.72±0.44	8.66±0.32	
Cobalt	Dry	14.62±0.25	59.27±0.43	37.25±0.52	15.10±0.25	38.55±0.37	29.68±0.49	56.41±0.55	50
	Wet	2.10±0.09	37.10±0.69	36.94±0.36	3.10 ± 0.17	34.65±0.43	38.03±0.39	29.09±0.49	
Copper	Dry	12.06±0.16	2.03±0,17	4.15±0.28	39.34±0.59	26.80±1.13	32.80±0.61	44.02±0.36	100
	Wet	22.72±1.54	50.82±1.48	29.12±0.81	43.57±1.25	67.49±1.31	63.3±0.91	137.24±12.16	
Iron	Dry	18315.79±284.27	16502.29±351.67	15395.62±300.57	19973.06±74.22	20040.41±132.04	13021.60±141.51	21080.01±184.74	50,000
	Wet	22057.25±144.94	19370.86±166.38	12975.65±97.56	20033.37±135.55	20312.59±218.21	15484.10±364.55	13384.49±174.55	
Chromium	Dry	2.73±0.15	8.40±0.10	4.37±0.15	5.30±0.10	8.13±0.21	7.97±0.15	8.10±0.20	100
	Wet	0.5±0.006	2.00±0.10	2.90±0.20	5.60±0.20	9.63±0.25	1.87±0.21	2.07±0.21	
Nickel	Dry	183.36±3.93	262.03±4.45	206.93±4.03	119.73±4.45	192.39±5.87	204.44±4.28	174.58±3.67	50
	Wet	75.87±1.01	86.64±1.98	89.39±1.85	82.73±1.69	121.35±1.26	132.01±1.32	78.02±1.35	
Lead	Dry	515.65±7.01	344.85±10.43	423.34±10.11	227.09±5.95	317.26±6.23	437.97±16.31	452.09±23.16	100
	Wet	9.89±0.56	18.32±0.66	12.80±0.59	7.86±0.59	14.96±0.51	16.27±0.34	14.69 ± 0.34	
Zinc	Dry	56.40±2.13	43.98±2.54	13.52±1.13	26.68±1.03	18.73±0.83	22.28±1.14	23.92±1.48	300
	Wet	48.37±1.66	54.17±1.75	42.80±1.38	30.97±1.11	37.70±0.49	30.70±1.52	33.17±1.00	

^{*} Bolded values indicate parameters that are above the WHO recommended limit

3.9 Pollution Indices

3.9.1 Geoaccumulation Index

Iron, Chromium and Zinc recorded negative I geo values in all the sampling stations during both the dry and wet seasons (class 0) signifying unpolluted sediment status. Cobalt registered negative I geo values at sampling points 1 and 4 during both the dry and wet seasons (class 0), therefore signifying unpolluted status. However, the I geo value for Cobalt at sampling point 2 and 7 reported moderately polluted status (class 2) during the dry season. All the remaining points reported unpolluted to moderately polluted status (class 1) during both the dry and wet seasons. The class 1 and 2 status of Cobalt in sediments may be attributed to dumping of paints, discharge of raw sewage and other Cobalt - rich wastes into the river. Copper registered negative I geo values (class 0) in all the sampling points, signifying unpolluted status. However, sampling points 6 and 7 recorded unpolluted to moderately polluted status (class 1) and moderately polluted status (class 2) respectively during the wet season. These pollution statuses can be attributed to surface runoff carrying pollutants rich in copper from construction sites and garages as well as from pesticides during the wet season. Lead registered unpolluted status (class 0) as signified by negative I geo values in all the sampling points during the wet season. However, the dry season saw a change in the recorded I geo values, ranging from strongly polluted (class 4) and strongly polluted to extremely polluted (class 5). This extreme pollution level can be linked to discharge of raw sewage into the river, dumping of solid wastes from garages, workshops and construction sites as well as the use of lead-rich pesticides and herbicides in farming. Nickel recorded unpolluted to moderately polluted status (class 1) at sampling points 1,2,3,4 and 7 during the wet season. However, sampling points 5 and 6 registered moderately polluted status (class 2) during the wet season. During the dry season, Nickel recorded moderately polluted status (class 2) in sampling points 1,3,5, 6 and 7 whereas sampling point 4 recorded unpolluted to moderately polluted status (class 1) and moderately polluted to strongly polluted status (class 3) at sampling point 2 during the dry seasons. These pollution statuses of Nickel can be linked to the discharge of raw sewage and dumping of solid wastes from garages and workshops into the river, leading to pollution by Nickel.

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Table 6: Geoaccumulation index values for sediments in river Ndambuk

Sampling Point	Season	Co	Cu	Fe	Cr	Ni	Pb	Zn
S1	Dry	-0.71	-2.32	-1.71	-5.34	1.61	4.34	-0.79
	Wet	-3.52	-1.40	-1.44	-7.79	0.34	-1.37	-1.01
S2	Dry	1.30	-4.89	-1.86	-3.72	2.13	3.76	-1.15
	Wet	0.63	-0.24	-1.63	-5.79	0.53	-0.48	-0.85
S3	Dry	0.63	-3.85	-1.96	-4.67	1.79	4.05	-2.85
	Wet	0.62	-1.04	-2.21	-5.26	0.58	-0.99	-1.19
S4	Dry	-0.67	-0.61	-1.59	-4.39	0.99	3.16	-1.87
	Wet	-2.95	-0.46	-1.58	-4.31	0.46	-1.70	-1.66
S5	Dry	0.68	-1.16	-1.58	-3.77	1.68	3.64	-2.38
	Wet	0.53	0.17	-1.56	-3.53	1.02	-0.77	-1.37
S6	Dry	0.31	-0.87	-2.20	-3.80	1.77	4.10	-2.13
	Wet	0.66	0.08	-1.95	-5.89	1.14	-0.65	-1.67
S7	Dry	1.23	-0.45	-1.51	-3.78	1.54	4.15	-2.03
	Wet	0.28	1.19	-2.16	-5.75	0.38	-0.80	-1.56

3.9.2 Contamination Factor

Iron, Chromium and Zinc recorded low contamination in all the sampling points during both the dry and wet seasons $(C_1 \le 1)$. Lead recorded low contamination $(C_1 \le 1)$ in all the sampling sites during the wet season, except at sampling point 2 which recorded moderate contamination (C_f = 1 - 3). During the dry season however, Lead registered very high contamination in all the sampling sites (C_f > 6), indicating pollution by lead. The use of lead rich pesticides and herbicides, coupled with raw sewage discharge and uncontrolled mining activities downstream is responsible for the high contamination factors witnessed. Copper recorded low contamination (C_f \leq 1) at sampling points 1 and 3 (both dry and wet seasons), sampling points 2, 4, 5 and 6 (dry season). However, points 2, 4 and 5 recorded moderate contamination during the wet season (C_f = 1 - 3), while point 7 recorded moderate contamination only during the dry season, but registered considerable contamination during the wet season ($C_f = 3 - 6$). Cobalt recorded low contamination during both dry and wet seasons at sampling points 1 and 4 ($C_f \le 1$), signifying minimal contamination from Cobalt. Sampling points 3, 5 and 6 registered moderate contamination during both the dry and wet seasons, whereas sampling points 2 and 7 registered moderate contamination only during the wet season. Considerable contamination was recorded at points 2 and 7 during the dry season. The high contamination at point 2 is due to the tributaries that bring in Cobalt rich contaminants from other parts of the sub catchment whereas the high contamination factor at point 7 is mainly due to uncontrolled mining activities downstream at the Kenya – Uganda border. Nickel registered moderate contamination at the first four sampling points during the wet season, while the remaining points registered considerable contamination with sampling point 2 recording very high contamination during the dry season. The high contamination level for Nickel can be attributed to discharge of raw sewage into the river, discharge of waste water by metal processing factory downstream as well as the mining activities downstream.

Table 7: Contamination factor values for sediments in river Ndambuk

Sampling Point	Season	Со	Cu	Fe	Cr	Ni	Pb	Zn
S1	Dry	0.91	0.30	0.46	0.04	4.58	30.33	0.87
	Wet	0.13	0.57	0.55	0.01	1.90	0.58	0.74
S2	Dry	3.70	0.05	0.41	0.11	6.55	20.29	0.68
	Wet	2.32	1.27	0.48	0.03	2.17	1.08	0.83
S3	Dry	2.33	0.10	0.39	0.06	5.17	24.90	0.21
	Wet	2.31	0.73	0.32	0.04	2.24	0.75	0.66
S4	Dry	0.94	0.98	0.50	0.07	2.99	13.36	0.41
	Wet	0.19	1.09	0.50	0.08	2.07	0.46	0.48
S5	Dry	2.41	0.67	0.50	0.11	4.81	18.66	0.29
	Wet	2.17	1.69	0.51	0.13	3.03	0.88	0.58
S6	Dry	1.86	0.82	0.33	0.11	5.11	25.76	0.34
	Wet	2.38	1.58	0.39	0.03	3.30	0.96	0.47
S7	Dry	3.53	1.10	0.53	0.11	4.37	26.59	0.37
	Wet	1.82	3.43	0.34	0.03	1.95	0.86	0.51

3.9.3 Pollution Load Index

Pollutants that arise as a result of anthropogenic activities can be determined using the pollution load index. Sampling points 1-4 registered no pollution due to anthropogenic activities during both the dry and wet seasons (PLI < 1); whereas sampling points 5-7 recorded pollution due to anthropogenic activities only during the dry season (PLI > 1) and lack of pollution due to anthropogenic activities during the wet season.

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Table 8: Pollution Load Index values of sampling points along river Ndambuk

Sampling Point	Season	PLI	
S1	Dry	0.93	
	Wet	0.30	
S2	Dry	0.97	
	Wet	0.72	
S3	Dry	0.72	
	Wet	0.58	
S4	Dry	0.91	
	Wet	0.46	
S5	Dry	1.12	
	Wet	0.88	
S6	Dry	1.13	
	Wet	0.72	
S7	Dry	1.37	
	Wet	0.72	

3.9.4 Enrichment Factor of Sediments in River Ndambuk

Chromium reported no enrichment in all the sampling sites during both the dry and wet seasons (E.F < 1). Zinc recorded no enrichment in sampling points 3, 5 and 7 during the dry season and at sampling point 4 during both the dry and wet seasons. All the remaining points registered minor enrichment (E.F = 1-3) during the dry and wet seasons. Cobalt registered no enrichment at points 1 and 4 during the wet season, but recorded minor enrichment and points 1 and 4 during the dry season. Moderate enrichment by Cobalt was recorded during at point 2 (wet season) and point 5 (dry and wet season). All the remaining points recorded moderately severe enrichment (E.F = 5 - 10) during both seasons. Moderately severe enrichment demonstrated by Cobalt can be attributed to the discharge of untreated sewage into the river, dumping of paint products as well as uncontrolled mining activities downstream. Copper recorded no enrichment status only at points 1,2 and 3 during the dry season, but registered minor enrichment at these points during the wet season. This shift in enrichment factor can be attributed to surface runoff carrying copperrich pollutants into the river during the wet season. Point 4 also recorded minor enrichment during the dry and wet seasons, but points 5 and 7 recorded minor enrichment only during the dry season, with the wet season registering moderate enrichment for points 5 and 6, with point 6 recording moderately severe enrichment during the wet season and point 7 recording severe enrichment during the wet season (E.F = 10 - 25). The severe enrichment status at point 7 can be attributed to the metal processing factory and uncontrolled mining activities downstream. Lead demonstrated minor enrichment at all the sampling points during the wet season, except point 4 which recorded no enrichment during the wet season. However, very serious enrichment was witnessed at points 2, 4 and 5 (E.F = 25 - 50) whereas points 1, 3, 6 and 7 recorded extremely

severe enrichment during the dry season (E.F > 50). This extremely high level of sediment pollution by Lead may be due to increased anthropogenic activities such as excessive use of pesticides and herbicides in farming, discharge of untreated sewage into the river, dumping of solid wastes such as paints and metals from garages and workshops as well as mining activities downstream. The extremely low pollution status by Lead during the wet season may be linked to dilution by rain water leading to reduced analyte concentration. The enrichment factor for Nickel was such that moderate enrichment was witnessed at points 1, 2 and 4 during the wet season, with the rest of the points recording moderately severe enrichment during the wet season. The dry season saw a shift in enrichment factor with points 4, 5 and 7 recording moderately severe enrichment during the dry season, whereas points 1, 2, 3 and 6 registered severe enrichment during the dry season. The drastic shift in enrichment factor between the dry and wet season can be linked to evaporation of water during the dry season leading to high analyte concentration, which is offset by rain water dilution during the wet season leading to a significant reduction in analyte concentration.

Table 9: Enrichment Factor Values for Sediments in River Ndambuk

Sampling Point	Season	Co	Cu	Cr	Ni	Pb	Zn
S1	Dry	2.00	0.66	0.08	10.01	66.24	1.89
	Wet	0.24	1.03	0.01	3.44	1.06	1.35
S2	Dry	8.99	0.12	0.28	15.88	49.17	1.64
52	Wet	4.79	2.62	0.06	4.47	2.23	1.72
S3	Dry	6.05	0.27	0.15	13.44	64.70	0.54
53	Wet	7.12	2.24	0.12	6.89	2.32	2.03
S4	Dry	1.89	1.97	0.14	5.99	26.75	0.82
54	Wet	0.39	2.18	0.15	4.13	0.92	0.95
S5	Dry	4.81	1.34	0.22	9.60	37.25	0.58
33	Wet	4.26	3.32	0.26	5.97	1.73	1.14
S6	Dry	5.70	2.52	0.33	15.70	79.14	1.07
	Wet	6.14	4.09	0.07	8.53	2.47	1.22
S7	Dry	6.69	2.09	0.21	8.28	50.46	0.70
31	Wet	5.43	10.25	0.08	5.83	2.58	1.53

3.10 Correlational Analysis

Only two metal pairs demonstrated strong correlation during the dry season. These are: Cr - Co (r = 0.72) and Ni - Co (r = 0.64). The strong correlations points to the existence of metal – metal complexes and alloys in sediments, especially stainless steel. Sediments act as reservoirs for pollutants, especially heavy metals, due to the high humus content in sediments which makes it easy for heavy metals to be adsorbed on the sediment's surface. A number of metal pairs demonstrated negative correlations during the dry season. They are: Co - Cd (r = -0.17), Cu - Cd (r = -0.68), Cd - Fe (r = -0.23), Cr - Cd (r = -0.78), Cd - Cd (r = -0.18), Cd - Cd (r = -0.18)

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0.22), Ni – Cu (r = 0.71), Zn – Cu (r = -0.37), Pb – Fe (r = -0.29), Ni – Fe (r = -0.54), Pb – Cr (r = -0.29) and Zn – Cr (r = -0.35). The negative correlation points to the absence of metal – metal complexes in sediments. During the wet season, the metal pairs which demonstrated strong correlation were: Pb – Cd (r = 0.84), Co – Cd (r = 0.87), Ni – Cd (r = 0.64) and Pb – Co (r = 0.88). The strong correlation between these metal – metal pairs points to the existence of metal – metal complexes and alloys in sediments. The metal pairs that showed negative correlation include: Fe – Cd (r = -0.15), Fe – Co (r = -0.59), Fe – Cu (r = -0.47), Zn – Cu (r = -0.46), Pb – Fe (r = -0.31), Ni – Fe (r = -0.08), Pb – Cr (r = -0.07), Zn – Cr (r = -0.33) and Zn – Ni (r = -0.39). This negative correlation signifies the absence of alloys in sediments during the wet season.

Table 10: Correlational analysis for heavy metals in sediments - Dry season

	Cd	Co	Cu	Fe	Cr	Pb	Ni	Zn
Cd	1.00							
Co	-0.17	1.00						
Cu	-0.68	-0.13	1.00					
Fe	-0.23	0.04	0.45	1.00				
\mathbf{Cr}	-0.78	0.72	0.33	0.00	1.00			
Pb	0.43	0.04	-0.22	-0.29	-0.29	1.00		
Ni	0.14	0.64	-0.71	-0.54	0.36	0.30	1.00	
Zn	0.24	-0.18	-0.37	0.07	-0.35	0.31	0.19	1.00

Table 11: Correlational analysis for heavy metals in sediments - Wet season

	Cd	Co	Cu	Fe	Cr	Pb	Ni	Zn
\mathbf{Cd}	1.00							
Co	0.87	1.00						
Cu	0.13	0.32	1.00					
Fe	-0.15	-0.59	-0.47	1.00				
Cr	0.34	0.10	0.06	0.26	1.00			
Pb	0.84	0.88	0.38	-0.31	-0.07	1.00		
Ni	0.64	0.56	0.03	-0.08	0.42	0.46	1.00	
Zn	0.24	0.05	-0.46	0.35	-0.33	0.25	-0.39	1.00

^{*}Bolded values show significant correlation

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4.0 CONCLUSION AND RECOMMENDATIONS

4.1 Conclusion

Cadmium, Nickel and Lead are the heavy metals whose concentration was above the WHO recommended levels in sediments. However, the concentration of Lead was above the WHO limit only during the dry season. Cobalt, Copper, Iron, Chromium and Zinc were below the WHO limit during both the dry and wet seasons. Iron, Chromium and Zinc recorded negative geoaccumulation index values, signifying no pollution. However, Lead showed strongly polluted status only during the dry season, with the wet season signifying no pollution by Lead. Sampling points 1 – 4 demonstrated no pollution due to anthropogenic activities but points 5 – 7 showed pollution due to anthropogenic activities as per the respective pollution load index values. Lead recorded low contamination factor values during the wet season, indicative of low contamination by Lead. However, the dry season saw a rise in contamination factor values with all the sampling points recording very high contamination. Nickel registered very high contamination at sampling point 2 during the dry season. Lead recorded minor enrichment in all the sampling sites during the wet season. However, the metal registered very serious to extremely severe enrichment during the dry season. Nickel recorded moderate enrichment to moderately severe enrichment during the wet season, but severe enrichment was registered during the dry season.

4.2 Recommendations

In view of the above, this study recommends the following measures to be put in place to curb soil and sediment pollution:

- Proper solid waste management systems should be adopted by both the County and National governments
- ii. Industrial effluents should undergo proper treatment before being discharged in soil and water bodies such as rivers
- iii. Materials such as paper, plastics, metals and glass should be recycled instead of being dumped in the open
- iv. Biological pest control should be adopted as an alternative to chemical pesticides
- v. Biodegradable wastes should be used to generate clean fuel such as biogas
- vi. Manures and other biofertilizers should be prioritized as an alternative to chemical fertilizers
- vii. The National Environment Management Authority (NEMA) should implement the law by prosecuting offenders who violate environmental safety laws
- viii. The environment policies need to be reviewed as some are not effective in controlling environment pollution.
- ix. Citizens should be capacity build on environment conservation and benefits of conserving the environment.
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