



Determining Heavy Metal Levels in Surface Water Samples from Selected Creeks in Rivers State, Niger Delta, Nigeria

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Abstract

Most of the trash that businesses and homes make, including heavy metals, ends up in the aquatic environment. Heavy metal pollution is still a big problem in the Niger Delta area of Nigeria when it comes to food safety. The study was done to find out the amount of heavy metals in surface water samples from some creeks in Rivers State, Niger Delta, Nigeria. In Rivers State, Nigeria, samples of surface water were taken from the creeks of Borokiri, Kaa, Okrika, and Eagle Island. Samples were analyzed using standard laboratory methods and an atomic absorption spectrometer (AAS) was used to find out the amounts of heavy metals. Both descriptive and inferential methods were used to analyze the results. In the study, the levels of heavy metals (in mg/l) in surface water were found to be: Cd (0.5186-3.6911), Cu (2.7160-5.9167), Zn (3.1172-6.5031), Cr (1.8972-5.3281), Ba (1.1169-2.8911), Pb (2.2874-4.8069), and Ni (1.9724-5.0691). The levels of heavy metals obtained in this study were above regulatory limits by the World Health Organization (WHO) and the Federal Ministry of the Environment (FMENV). The elevated levels of heavy metals recorded may have come from sewage treatment plants, sewage flows, building sites, illegal oil bunkering and runoff from farms in the study areas. The high amounts of heavy metals in the surface water in the study areas could be harmful to aquatic life and even humans if they eat these contaminated aquatic animals. The results show that there is a significant difference in the amounts of heavy metals in the surface water at the different sites. To stop the Creeks from getting worse from heavy metals, it is suggested that relevant authorities should monitor and control the random dump of household and commercial wastes, as well as untreated wastewater from factories, into the rivers.

Keywords: Heavy Metals, Aquatic Environment, Pollution, Permissible Limits, AAS.

Introduction

The majority of human-made waste, including heavy metals, ends up in aquatic environments. The Niger Delta region of Nigeria is currently experiencing a worrying amount of heavy metal poisoning in the aquatic environment, which is a rapidly growing problem globally (Osa-Igwehide et al., 2016). This is significant since, according to Kpee and Ekpete, (2014), Nigeria is not considered one of the world's industrialized nations. According to several studies (Kpee & Ekpete, 2014; Nwineewii et al., 2018; Khan et al., 2004; Merian, 1984), heavy metals can come from a wide range of human activities, including sewage drainage, fertilizer use, mining, increased industrialization and urbanization, and even oil spills. In contrast, metals are present in nature in trace amounts and can enter water sources by leaching from rocks, dust in the air, forest fires, and plants. Heavy metals are present in aquatic environments permanently because they do not break down but instead collect and integrate with water and aquatic creatures (Mora et al., 2005). Heavy metal contamination results from this. Environmentalists are increasingly concerned about the increasing concentration of heavy metals in the environment as a result of human activities (Opeolu et al., 2008). When discharged into the environment, metals tend to accumulate in living tissues through the food chain, unlike dangerous chemical compounds that can often be broken down (Cossica et al., 2002). The bulk of Nigeria's industrial sectors generate waste, which is frequently disposed of without giving any thought to environmentally sound waste management practices. Both small and large-scale industries have this trait. The majority of the waste created is transported into rivers via surface runoff. This largely leads to the poisoning of natural water sources and the overall environment (Adesemoye et al., 2006). According to Ogedengbe and Akinbile, (2004), industrial waste is the leading cause of water contamination in modern times. Heavy metals are generally recognized as environmental dangers

because of their extreme toxicity, long-lasting presence in the environment, and potential to accumulate in living beings. Decomposition of metal-containing rocks and volcanic eruptions are two naturally occurring sources of metal pollution. Metal contamination is exacerbated by human activities such as mining, industrial operations, and agricultural practices (Ali et al., 2019). Both terrestrial and marine ecosystems are greatly threatened by trace metals that have hazardous effects. After being released from both natural and man-made sources, heavy metals contaminated soils, sediments, and water sources. Pollutants from industries and volcanic eruptions both contribute to heavy metals in the atmosphere, which recirculate and contaminate land and water (Masindi & Muedi, 2018). Heavy metals are so long-lived that they eventually end up in living things or leak into the groundwater. Significant implications for human health arise from the presence of heavy metals in both living things and subterranean water. Heavy metals can have devastating consequences on aquatic life, even in trace amounts. These substances have the potential to cause significant histopathological alterations in fish and other aquatic animals' tissues. The pollution of water bodies with heavy metals is caused by a multitude of things. Heavy metals in water sources are largely due to mining effluents. Heavy metal poisoning of water sources can also be caused by a variety of industrial discharges, wastewater from homes, and runoff from farms. One major source of surface and groundwater contamination is the discharge of untreated industrial effluents into water bodies (Zeitoun & Mehana, 2014).

Heavy metal toxicity is a major concern because of the numerous health risks it is linked to. When it comes to human biology, these metals are practically insignificant. However, their poisonous qualities can cause systems in the body to malfunction. Occasionally, these elements can act as if they were part of the body, causing metabolic processes to malfunction. As they accumulate in the body, chronic diseases can set in. To protect the public's health, steps have been taken to control and prevent metal toxicity, which can develop from various sources such as the workplace, accidents, and the environment (Kuepper & Kroneck, 2005). How much metal is absorbed, how it is exposed, and for how long all contributes to a metal's toxicity. By forming unintended bonds with protein sites, these heavy metals displace the original metals from their proper binding locations. The hazardous effects of the heavy metals cause cell dysfunction as a result of this displacement. Heavy metal interactions with nuclear proteins and DNA are the principal drivers of oxidative degradation of biological macromolecules. Heavy metal salts, acids, organic matter, pesticides, and cyanides are just a few of the dangerous substances found in industrial waste. These substances degrade the physical and chemical properties of water. These pollutants have a domino effect on aquatic life, killing off species as they move up the food chain (Jaishankar et al., 2014). The purpose of this research is to determine the levels of cadmium, copper, zinc, chromium, barium, lead and nickel present in the surface water of various rivers and creeks in the Nigerian state of Rivers. The level of compliance will be determined by comparing the obtained data to national and international standards.

Materials and Methods

The research was carried out in Rivers State in the Niger Delta, Nigeria, around the Okrika, Borokiri, Eagle Island, and Kaa creeks respectively. The rivers in the study area receive waste discharges from industries situated along its banks. In the study area, a lot of anthropogenic activities such as dredging, construction, water transportation, illegal oil bunkering, commercial farming, and fishing take place.

Table 1: Coordinates of Sampling Areas

	Locations			
	Okrika	Borokiri	Eagle Island	Kaa
Latitude	4°43'53.58"N	4°45'24.39"N	4°47'10.62"N	4°34'10.86"N
Longitude	7°4'36.52"E	7°1'31.98"E	6°58'36.68"E	7°22'9.97"E

Collection of surface water samples for heavy metals analysis

Water samples for the study were collected with pre-cleaned bottles from four different rivers (creeks) against the flow of the rivers at a depth of 20-30cm below the water surface. Samples were immediately treated with two drops of concentrated nitric acid (HNO₃ analytical grade). Samples were well labelled for identification and stored in an iced cooler in the sampling locations and then transported to the laboratory for pre-treatment, determination and analysis. Samplings were done between January and February 2021.

The surface water samples underwent heavy metals analysis using the Solar Thermo Elemental Atomic Absorption Spectrophotometer (AAS) model SN.SG-710960. Analytical testing was conducted on both the sample solution and

the blank reagent to determine the presence of seven heavy metals, namely Cadmium (Cd), Copper (Cu), Zinc (Zn), Chromium (Cr), Barium (Ba), Lead (Pb), and Nickel (Ni).

The concentrations obtained from the analyses were recorded as the mean ± standard deviation (SD). The collected results were analyzed using descriptive and inferential statistics. More precisely, the statistical measures of mean, standard deviation, and t-test were employed. Statistically significant results were defined as those with probabilities less than 0.05 ($p < 0.05$).

Results

This study determined the levels of heavy metals in surface water samples collected from four different creeks in Rivers State. Samples were analysed using standard analytical techniques and results obtained are presented in Table 2.

Table 2. Concentrations (mg/l) of heavy metals in surface water from various sampling stations

Sampling Stations	Cd	Cu	Zn	Cr	Ba	Pb	Ni
Okrika Creeks	3.6911	4.9172	6.5031	3.7067	2.8911	3.1672	4.9172
Borokiri Creeks	2.8748	5.9167	4.8147	5.3281	1.1872	4.8069	5.0691
Eagle Island creeks	0.5186	3.8716	5.0069	4.8911	2.1692	2.2874	3.4172
Kaa/Khana Creeks	1.9107	2.716	3.1172	1.8972	1.1169	3.0912	1.9724
Mean ± SD	2.249±1.364	4.355±1.375	4.860±1.386	3.956±1.534	1.841±0.849	3.338±1.057	3.844±1.453
WHO Permissible Limits	0.003	2	3	0.05	1	0.025	0.02
FMENV	0.01	0.01	0.2	0.3	NA	0.1	0.1

NA=Not Available; FMENV=Federal Ministry of Environment.

Table 3. Descriptive statistics of the concentrations of heavy metals in surface water

Metal	N	Range	Minimum	Maximum	Mean	SD	Variance
	Statistic	Statistic	Statistic	Statistic	Statistic	Std. Error	Statistic
Cd	4.000	3.173	0.519	3.691	2.249	0.682	1.860
Cu	4.000	3.201	2.716	5.917	4.355	0.688	1.892
Zn	4.000	3.386	3.117	6.503	4.860	0.693	1.920
Cr	4.000	3.431	1.897	5.328	3.956	0.767	2.353
Ba	4.000	1.774	1.117	2.891	1.841	0.424	0.721
Pb	4.000	2.520	2.287	4.807	3.338	0.528	1.117
Ni	4.000	3.097	1.972	5.069	3.844	0.727	2.113

Table 4. One sample T-test of heavy metal concentrations in surface water

Metal	t	df	Sig. (2-tailed)	Test Value = 0		
				Mean Difference	95% CI	
				LB	UB	
Cd	3.298	3.000	0.046	2.249	0.079	4.419
Cu	6.333	3.000	0.008	4.355	2.167	6.544
Zn	7.015	3.000	0.006	4.860	2.655	7.065
Cr	5.158	3.000	0.014	3.956	1.515	6.396
Ba	4.337	3.000	0.023	1.841	0.490	3.192
Pb	6.317	3.000	0.008	3.338	1.656	5.020
Ni	5.289	3.000	0.013	3.844	1.531	6.157

Discussion

Levels (mg/l) of heavy metals in surface water

The levels of heavy metal in the surface water collected from the different creeks are presented in Table 2.

Cadmium (Cd):

The levels of cadmium (Cd) in surface water samples from the various sampling locations measured between 0.5186 and 3.6911 mg/l, with a mean ± standard deviation of 2.249 ± 1.364 . Eagle Island had the lowest concentration of cadmium, whereas Okrika had the highest concentration of the element. According to the World Health Organization (WHO), (2006) and the FMENV, (1991), the concentration that was obtained was greater than the authorized limit of

0.003 mg/l and 0.03 mg/l, respectively. The high amount of cadmium that was discovered in the surface water of Eagle Island, Borokiri, and Okrika could be attributed to human activities such as industrial effluents, continual dredging and construction in the region, and other human activities. The quantities of cadmium that have been introduced into Kaa Creek might be attributed to the presence of construction sites, dredging operations, and the disposal of domestic garbage that are located in the vicinity. Nwineewii et al. (2019) recorded a concentration of 0.0085 ± 0.003 mg/l for the New Calabar River in Rivers State, Nigeria. Okoya et al. (2020) reported a range of 0.004 - 0.027 mg/l (0.02 ± 0.00) for water near the Ikirun Iron smelting business in Osun State, Nigeria. In addition, Okoya et al. (2020) observed a concentration of 0.004 - 0.027 mg/l (0.02). This investigation found that the concentration of cadmium that was collected was more than the levels that were reported in previous studies in the Oge-Etche River, located in Etche, Rivers State, Nigeria, and in the surface water of Odeama village, located in the Niger Delta of Nigeria, respectively, Edori et al. (2023) and Okoro and Diejomaoh, (2022) discovered low quantities of cadmium, with values ranging from 0.0246 ± 0.018 mg/l to 1.5386 ± 0.051 mg/l. Studies have shown that high amounts of cadmium in water can induce renal illness, lung damage, skeletal fragility, and structural changes in enzymes that restrict their catalytic function (Nwineewii & Momta, 2022; Uzamere et al., 2023). These effects can be severe enough to cause kidney disease.

Copper (Cu):

Copper (Cu) concentrations in surface water samples from the various sampling locations varied from 2.7160 to 5.9167 mg/l with a mean \pm SD = 4.355 ± 1.375 . The surface water from the Borokiri stream had the greatest percentage of copper, which is most likely the result of human activity in the region, such as the illegal bunkering of oil and the dumping of garbage from both home and commercial sources. This is in contrast to the surface water from Kaa Creek, which had the lowest concentration of copper. This may be the result of the accumulation of rubbish from homes that has been thrown into the river as well as runoff from agricultural farms that are located nearby. In Okrika, the copper concentrations that were recorded can be linked to the discharge of effluents from the refinery as well as the continuing dredging works that are taking place in the study areas. It is possible to establish a relationship between the concentration of copper that was recorded in Eagle Island and the current dredging and construction operations that are taking place in the study area. The concentration that was obtained in the present study was higher than the concentration that was reported from the New Calabar river in Rivers State, Nigeria (Nwineewii et al., 2019) and the surficial water of the Silver River in Southern Ijaw, Bayelsa State, Nigeria (Ekpeta et al., 2019). Oguzie and Okhagbuzo reported in 2010 that the concentration of copper in the Ikpoba River in Benin City, Nigeria, was measured to be 0.043 mg/l. The obtained concentration of copper in the present study is higher than the maximum permitted limits of 2 mg/l (as declared by the World Health Organization in 2012) and 0.01 mg/l (as indicated by the Food and Drug Administration in 1991). Edori and Iyama (2020) conducted research in which they analyzed the levels of copper pollution in water samples that were obtained from Edagberri Creek in Engenni, which is located in Rivers State, South-South, Nigeria. Plants and animals both require copper to grow and develop properly. Copper is an essential element. When it comes to the creation of haemoglobin in human blood, it is an extremely important factor. According to Nwineewii and Momta (2022), consuming an excessive amount of copper can lead to anaemia, as well as probable damage to the liver and kidneys, as well as irritation of the stomach and intestines.

Zinc (Zn):

There was a variation in levels of zinc in the surface water samples that were collected from different sampling locations in the rivers. The zinc concentrations varied from 3.1172 mg/l to 6.5031 mg/l, with a mean \pm SD value of 4.860 ± 1.386 . These values are greater than the recommended limits that were established by the World Health Organization (WHO) in 2006 (3 mg/l) and the FMENV in 1991 (1.0 mg/l), respectively. Kaa had the lowest amounts of zinc and chromium, whereas Okrika Creek and Borokiri had the largest quantities of these elements. Kaa had the lowest levels of these elements. The greatest amounts were found in Borokiri Creek and Okrika Creek respectively. The elevated levels of zinc that were discovered in the water samples that were collected from the Kaa and Borokiri rivers could have been caused by several factors, including the presence of a metal boat that had been abandoned in the river, activities associated with local dredging, the illegal transit of oil bunkering via the river, and active construction projects in the surrounding area. The extraordinarily high amounts of zinc that have been seen on Eagle Island and Okrika can be linked to the presence of construction, dredging, and industrial operations that are located near the river bank. Compared to the range of 5.167 ± 0.63 mg/l to 8.239 ± 2.41 mg/l that was reported by Ekpeta et al. (2019) in the surface water of Silver River, Southern Ijaw, Bayelsa State, Nigeria, and 0.19 ± 0.64 mg/l (0.48 ± 0.13 mg/l) in the surface water of an oilfield in the Niger Delta (Howard et al., 2005), the value that was obtained in the current

study was found to be lower. The findings of this study, on the other hand, suggested a higher value when compared to the findings that were given by Okoya et al. (2020) for water samples taken around the Ikirun Iron smelting factory in Osun State, Nigeria, as well as the data that were supplied by Nwineewii et al. (2019) for the New Calabar River. Both of these studies were conducted in Nigeria. Zinc may be found in its natural condition in the dirt, water, and air. It is also possible to locate it in the atmosphere. Furthermore, an excessive amount of zinc may be hazardous and lead to poor implications for one's health (Nwineewii & Momta, 2022). Zinc is needed for the maintenance of a healthy body; nevertheless, an excessive amount of zinc can be harmful. It has been demonstrated that zinc (Zn) has a detrimental effect on microbes, plants, and animals, as stated by Rout and Das, (2003) and Muysen et al. (2006).

Chromium (Cr):

The levels of chromium that were discovered in the surface water ranged from 1.8972 to 5.3281 mg/l, with a mean \pm SD value of 3.956 ± 1.534 . This value is comparable to the one the results obtained by Ekpete et al. (2019) in the Surficial water of Silver River, Southern Ijaw, Bayelsa State, Nigeria, and Marcus and Edori, (2016) in Bomu and Oginigba River, Rivers State, Nigeria. However, it is higher than the mean range of 4.6070 ± 0.284 mg/l to 6.2551 ± 0.241 mg/l in the Oge-Etche River, Etche, Rivers State, Nigeria (Edori et al., 2023). Nwineewii et al. (2019) revealed that the water from the New Calabar River in Port Harcourt, Nigeria, has a low amount of chromium (Cr) with a concentration of 0.69 ± 0.692 mg/l. In this particular investigation, the concentration of Cr was found to be greater when compared to the recommended limit of 0.05 mg/l (WHO, 2012) and the suggested value of 1 mg/l (FMENV, 1991). Several factors might be responsible for the concentration of Cr that was found in water samples taken from the Kaa River (Ghani, 2011; Mohammad et al., 2020). These factors include the transportation of illegal oil bunkering, agricultural runoff, and construction activities that are taking place in the region. Alteration of genetic material, as well as gastrointestinal distress, seizures, haemorrhage (Nwineewii & Edem, 2014), and ulceration, are all symptoms of Cr.

Barium (Ba):

The concentration of barium (Ba) varied from 1.1169 to 2.8911 mg/l, with a mean value of 1.060 mg/l and a standard deviation of 0.400 mg/l. All of these values were relative to one another. A limit of 1000m/l has been established by the World Health Organization (WHO), and this level is more than that limit. The sample of surface water that was obtained from Okrika Creek contained the highest amount of barium (Ba) that was found. There may be a connection between this and the expulsion of garbage from the refinery. On the other hand, Kaa had the lowest concentration. In the research that Okoro and Diejomaoh, (2022), they reported that the level of Ba in the surface water of the Odeama village, which is located in the Niger Delta of Nigeria, was less than 0.005 mg/l. Barium is most commonly found in the form of the minerals barite (BaSO_4) and witherite (BaCO_3). The electrolysis of barium chloride (BaCl_2) is the primary method for producing barium. Water softening is accomplished by the utilization of barium chloride. Barium can cause several health problems when it is taken in very small doses. The following are some of the symptoms that may be experienced: breathing issues, high blood pressure, alterations in the rhythm of the heart, irritation of the stomach, muscular weakness, swelling of the brain, damage to the liver, and poor kidney and heart function (Nwineewii & Momta, 2022).

Lead (Pb):

There was a wide range of lead concentrations found in the surface water samples, with a mean value of 4.438 ± 0.848 mg/l. The lead values ranged from 2.2874 mg/l to 4.8069 mg/l. These values are greater than 0.025mg/l (WHO, 2012) and 1.0mg/l (FMENV, 1991) regulation limits. Edori and Iyama, (2020) conducted research that evaluated the presence of heavy metal contamination in the water of Edagberi Creek, which is located in Engenni in Rivers State, South-South, Nigeria. The findings of the study, when compared to the findings of the present research, indicated that the levels of lead that were tested were lower than the requirements for drinking water that were established by the World Health Organization and the National Agency for Food and Drug Administration Control (NAFDAC). According to the findings of the study, surface water samples taken from Borokiri were shown to have the highest amounts of lead. There is a possibility that this is a result of the transportation of illegal oil bunkering activities and construction projects that are now taking place in the region. According to the results of this investigation, the average concentrations of lead in the surface water samples that were analyzed were equivalent to the range of values that were reported by Edori et al. (2023), which had values ranging from 3.0057 ± 0.040 mg/l to 4.4311 ± 0.135 mg/l. However, when compared to the values that were published by Nwineewii et al. (2019) and Ekpete et al. (2019), these values were much greater than what was reported by those other researchers. Not only does lead poisoning affect the

central nervous system, but it also affects the gastrointestinal tract, as stated by Markowitz, (2000). Some of the symptoms that may appear soon after exposure to the chemical include a decrease in appetite, headache, high blood pressure, stomach discomfort, renal malfunction, weariness, inability to sleep, and inflammation of the joints. On the other hand, long-term exposure can lead to cognitive impairment, congenital malformations, decreased body mass, immobility, muscular debility, brain damage, renal impairment, and potentially even death (Marin & Griswold, 2009). These adverse effects can be caused by exposure to the substance over an extended period.

Nickel (Ni):

Nickel concentrations ranged from 1.9724-5.0691 mg/l, with a mean \pm SD value of 4.261 \pm 1.139 mg/l. Nickel concentrations were found to be variable. The value that was recorded in this study is greater than the allowed limit that was set by the WHO, (2012) which is 0.02 mg/l, as well as the limit (1.0mg/l) that was established by the FMENV, (1991). Ni was found to have the greatest levels in surface water samples that were obtained from Borokiri Creek. This may be the outcome of the construction and oil bunkering operations that are taking place in the region. Nevertheless, the surface water samples that were collected from Kaa Creek had the least amount of the chemicals that were studied. Edori and Iyama, (2020) investigated to determine the levels of heavy metals in the water of Edagberi Creek, which is located in Engenni, Rivers State, South-South, Nigeria. But. When compared to the findings of the current research, the findings of the study revealed that the levels of nickel that were observed were greater than the permissible limit that was established by the World Health Organization and the NAFDAC for drinking water. The concentration of nickel that was discovered in this study is distinct from the concentration that was reported in the surface water of the Silver River in Southern Ijaw, Bayelsa State, Nigeria (Ekpete et al., 2019) and in the Oge-Etche River in Etche, Rivers State, Nigeria by Edori et al. (2023). Both of these studies were conducted in Nigeria. On the other hand, it beats the average concentration of 1.58 \pm 1.26mg/l that was obtained in the New Calabar River in Port Harcourt, Nigeria (Nwineewii et al., 2019) and the concentration of 0.091mg/l that was recorded in the Ikpoba River in Benin City, Nigeria (Oguzie & Okhagbuzo, 2010). The element nickel is classified as a trace element, which indicates that it is present in the environment in extremely minute quantities and is required in extremely minute levels. Excessing the maximum permissible quantity of nickel may be damaging and can lead to the development of numerous different forms of cancer (Valko et al., 2005) in various regions of the bodies of animals. This is in addition to the fact that it can cause difficulty in breathing and other health concerns. To determine whether or not there was a statistically significant difference in the quantities of heavy metals that were discovered in the various sampling locations, the results of a one-sample t-test were assessed. According to the data shown in Table 4, it can be observed that there were differences in the amounts of all heavy metals in the surface water samples that were collected from various sampling sites. These variations were found to be statistically significant ($p < 0.05$). To be more specific, the p-values for the elements Cd, Cu, and Zn were accordingly 0.046, 0.008, and 0.002 respectively. More specifically, the p-values for Cr, Ba, Pb, and Ni were respectively 0.014, 0.023, 0.008, and 0.013.

Conclusion

This study quantified the levels of heavy metals present in the surface water. The study's findings unambiguously demonstrate the concentrations of these toxic heavy metals. The levels of heavy metals Cd, Cu, Zn, Cr, Pb, Ba, and Ni in surface water are significantly higher than the allowed limits set by the World Health Organization (WHO) and the Federal Ministry of Environment (FMENV). The presence of high concentrations of heavy metals in the surface water of the study areas may pose a risk to aquatic organisms and could potentially be transferred to humans through the consumption of contaminated aquatic organisms. This could lead to both carcinogenic and non-carcinogenic health effects in individuals exposed to these contaminants.

Recommendation

Due to the high concentrations of heavy metals found in the study areas, it is advisable for the appropriate authorities to closely monitor and control the careless disposal of domestic and commercial waste, as well as untreated industrial effluents, into the rivers. This is necessary to prevent any additional heavy metal pollution in the Creeks.

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