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Level of Some Heavy Metal Contamination of Water and Sediments of River Pil-Gani Plateau State Nigeria

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Abstract: *Background:* River Pil-gany water just like any other is put to several uses, including human consumption. Recently, contamination and pollution of water resulting from human activities have greatly threatened the quality of water; to a point that despite the abundance of water, its availability for use is challenged. It is therefore pertinent to ascertain the quality of water bodies that have found varied uses and are surrounded by potential contamination sources. *Objective*: The objective therefore was to ascertain, compare and establish the level of contamination of the water and sediment of Pil-gany with respect to selected heavy metals. *Method*: The seasonal quality of river Pil-gany; water and sediment was assessed with regards to potential toxic heavy metals, using Atomic Absorption Spectrophotometry (AAS), through sample digestion and analysis. *Results*: The metals were assessed for samples obtained in December, 2018 and in August, 2019, and they included; Cd, Cr, Cu, Fe, Mn, Pb and Zn. The analysis of water samples obtained from different sampling points (Angwan Tabo, Gongani, Pishe, and Zamadede), in rainy and dry seasons, gave heavy metal concentrations in the following ranges; Cd (<0.001 - 0.003), Cr (0.070 - 1.983), Cu (<0.002 – 0.003), Fe (<0.003 - 0.882), Mn (0.005 - 0.477), Pb (0.01 – 1.097), Zn (<0.021 - 0.024), all in mg/L. On the other hand, the sediment thereof was found to contain the potential toxic heavy metals at different sampling units; (Angwan Tabo, Gongani, Pishe, and Zamadede), in rainy and dry seasons; in the following ranges; Cd (1.190 – 7.540), Cr (4.730 – 20.803), Cu (4.760 – 10.500), Fe (1744.000 – 8349.327), Mn (266.000 – 373.830), Pb (0.003 – 277.000), Zn (12.200 – 19.900), all in mg/L. *Conclusion*: All elements tested for, were detected in water samples obtained during rainy season though, at higher concentrations compared to those obtained during dry season. From the forgoing, some metals were detected only or rather in higher concentrations during rainy season; this might be that they were freshly washed in. The potential toxic metals present in the sediment were also present in the water. Variations were observed in their contents, in which cases some were above while other below the permissible limit set by regulatory bodies (NOAA/WHO). This may be attributed to adsorption capacity of the metals to the sediment, influx from originating sources in case of non-deposit contamination as well as topography of the river. The water body is generally regarded as not safe for consumption particularly for drinking; following its contamination and potential re-contamination from sediment-to-water transfer of toxic metals.

Keywords: Heavy Metals, Contamination, Atomic Absorption Spectrometry

1. Introduction

Water is a topmost precious and invaluable resource that is inevitable for the survival of man and many other forms of life on earth, forming an important and necessary fraction of their composition. It is found in great abundance, covering the earth surface with a whopping 70 percent and more [12]. River water is put to use in several ways, these include; human consumption, farming, recreation and as habitat to a wide spectrum of organisms. Water contamination and pollution resulting from leaching of natural element deposits and man's interferences therewith; have greatly threatened the quality of water; to a point that despite the abundance of water, its availability for use is challenged [15]. Anthropogenic activities' contribution to water contamination/pollution greatly outweighs those of natural origin [15]. As far back as 2017, Hadiza and Hindatu, reported that, the readily available sources of water to the local people of Nigeria are rapidly being severed by anthropogenic factors, of which pollution remains topmost [7]. Water pollution is regarded as a global challenge however, with greater bearing on developing countries, which is as a result of increase in industrialization and poor environmental sanitation practices [21]. Water pollution is a matter of great concern. A threat to water is a threat to life [12]. River water has remained eminently key in meeting the water needs of man, other animals, plants and industries. This has underscored the pertinence to protect it from any form of contamination and subsequent pollution. Hence, there is need to recurrently assess the quality of consumable waters for informed policy decisions for protection of life.

In recent times, heavy metals have emerged as pollutants of great concern; this is due to their rampantly common presence in industrial and technological wastes, showing wide array of toxicity and causing great damage to the environment, plants and animals. Although, some of these metals are micronutrients but at higher concentrations, they are toxic to animals, plants and aquatic lives [5]. Heavy metal toxicity is a function of its elemental species and chemical composition; for some of the metals, the most dangerous forms are those coupled to organic moieties, since, they are soluble in animal tissues and can pass through biological membranes. To man, the effects are endless however, famous toxicity is seeing in their attack on the central nervous function, leading to mental disorder and lungs, kidney, liver, blood composition and other important organs, causing serious damage [1].

Heavy metals are metals and metalloid elements that have specific density above 5 $g/cm^{3,}$ and relative atomic weight higher than 40.04. These elements are toxic even in trace amounts and they include but not limited to the following; Cd, Cu, Cr, Fe, Mn, Ni, Pb, and Zn.

Metals exist naturally and in different spheres of the earth; they are present in the atmosphere, earth crust, waters, soils/sediments and rocks and can also bio-accumulate in plants and animals [16]. However, as earlier mentioned, human industrial activities do cause the release of these heavy metals from the aforementioned natural housing into other sections of environment, originally with lesser concentrations of such metals leading to environmental pollution [22].

The entry of these heavy metals pollutants into the atmosphere, water, soil and sediments therefore, deleterious health effect in man, other organisms and the environment itself [11]. Heavy metal toxicity majorly depends on the relative oxidation state of the heavy metals. The multiple oxidation states of the metals support the efficacy in their binding to many biological molecules which include; proteins, enzymes, and DNA, among other, forming very stable bio-toxic chemical substances, which cause many physiological bio-toxic effects [11].

The potential toxic heavy metals of concern in the course of this study are herefore, highlighted below:

Cadmium (Cd), one of the non essential heavy metal elements is highly toxic [4]. It emerges from the by-product of zinc production and also found in phosphate fertilizers, which eventually gets washed into the water bodies [10]. Cadmium has extensive technological and industrial applications, hence found almost everywhere in the environment and is recognized as one of the most dangerous trace element as it shows a high soil to plant transference rate [10]. It also has tendencies to damage kidney at high concentration or bioaccumulate.

Chromium is an essential metal element for organism only in trace amounts as nutrients in form of fat and carbohydrate metabolism [9]. Furthermore, hexavalent chromium and Cadmium among other heavy metals have been declared carcinogenic by the International Agency for Research on Cancer (IARC) hence, may lead to cancer at higher concentrations [13].

Copper contamination of drinking water at high concentrations may lead to chronic anemia, it also accumulates in liver and brain and the major cause of Wilson's disease [18]. More also, Cu bio-accumulates in many organs of the body, causing hepatic and neurological disorders, some of which include; hepatitis, cognitive or psychiatric impairments and motor deficits [6].

Iron is the second most abundant element in the earth crust and has found extensive domestic, agricultural and other industrial uses, making it almost the most common element in the environment and due to ease of rust it gets easily washed into streams and other water bodies [6]. Even though, iron is an essential metal and do support many biological processes; in some instances, it acts as coenzyme such as in Hemoglobin and Myoglobin, it however, poses toxicity threat at higher concentration, in one instance, it is implicated as increasing potential risk of cancer of the lung [19].

Manganese is also toxic in higher concentrations; such that it bio-accumulates in the mitochondria, disrupting the ATP synthesis [1].

Lead has no nutritional benefits and it is a cumulative toxic heavy metal, which majorly affects the kidney, nervous hematopoietic and gastrointestinal systems, as well as male and female reproductive organs [10]. Furthermore, its environmental exposure has been associated with slight deficits in attention span and learning abilities and in dire cases, brain cancer.

Zinc is an important trace heavy metal; it supports many physiological and metabolic processes in many organisms [18]. Despite its importance, zinc at higher concentrations can be toxic with even fatal consequences [6]. Aside the human toxicity impact, the presence of heavy metals within water bodies above permissible limits have dangerous impact on the aquatic life, risking the health of the organisms to dire extent; killing the organisms. Otene *et al.*, reported that the loss of eco-diversity, reduction in productivity and the alteration of habitats are some of the challenging effects of these pollutants [17].

2. Method/Procedure

2.1. Collection and Preparation of Water and Sediment Samples

The water was sampled using 500 cm^3 transparent glass bottles for digestion and subsequent analysis, at a depth of 30 cm below the surface, with the help of graduated rope. The samples were thoroughly mixed in plastic bottles to ensure homogeneity and properly labeled. They were acidified with concentrated HNO_3 in order to keep the pH of the samples low; preventing precipitation of the metals, before being transported to the laboratory. The method of digestion reported by Edokpayi [3] was followed after which the samples were stored at 4°C in a refrigerator in order to maintain the integrity of the water samples prior to Analysis (AAS analysis).

On the other hand, sediment samples were collected at different sampling points, thereafter, air dried, homogenized, ground gently and sieved with 500 µm sieve before digestion. Sampling, digestion and analysis of the sediments for heavy metals were all done in accordance with the method developed by the United State Environmental Protection Agency.

2.2. The Study Area

Samples were collected at four different points at about 2-3 km intervals along River Pil-gani, Kafel Langtang North Metropolitan area, as shown in Figure 1. The sampling stations include; Angwan tabo, Gwongani, Pishe and Zamadede. At each sampling point and season (rainy and dry), water and sediment samples were collected for analysis. Several anthropogenic activities with tendencies to pollute the environment with heavy metals are present around the locale.

These include; agricultural activities, human settlements, medical facilities, waste dump sites and effluent from waste water treatment, among others. This is alongside the different metals deposit observed around the locale.

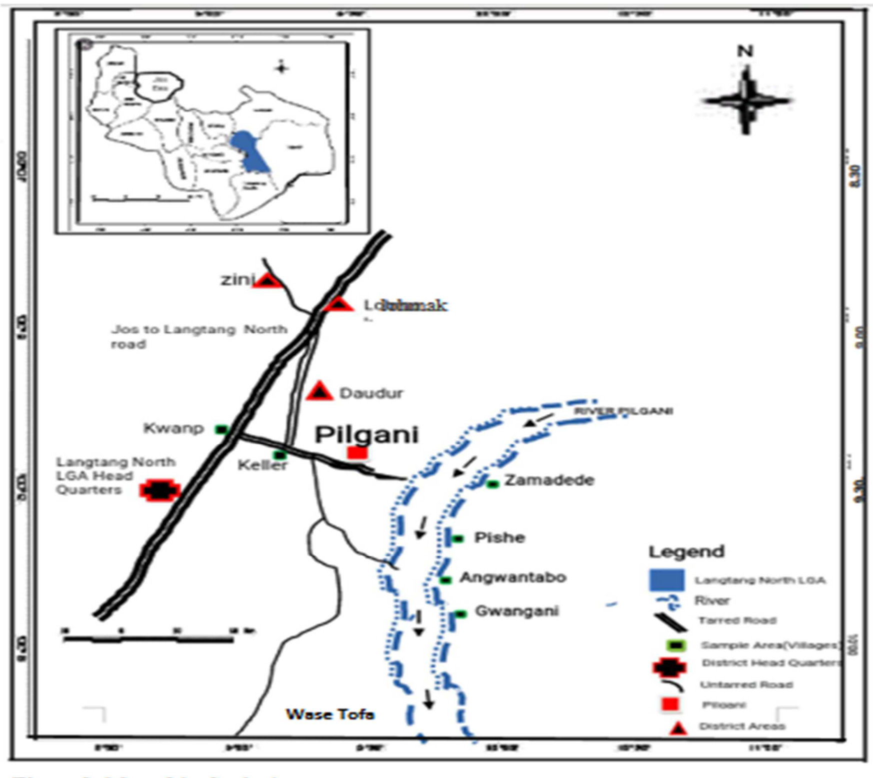

Figure 1. *Map of the Study Area (Source: kontrety kieta.com).*

2.3. Statistical Analysis

The data obtained in the course of the study was further analyzed statistically using SPSS version 20.0. One way analysis and multiple comparisons (Tukey post hoc test) were used to ascertain the levels of variations of the metals in the different sampling points and the seasons. The 95 % confidence level was invoked in declaring the significant differences within the compared groups.

3. Results and Discussion

Heavy Metals Levels in Water and Sediment Samples of River Pil-Gani in Rainy and Dry Seasons

The amount of heavy metals present in water is greatly influenced by biological uptake, release from sediments, scavenging by particulate matter, advection and Aeolian transport [8]. The best and most important step in preventing heavy metal poisoning is determination of the level of contamination, source and remediation [19]. From the foregoing, selected heavy metals were examined for their contamination and subsequent pollution of the studied water body and the sediment thereof, they include: Cd, Cr, Cu, Fe, Mn, Pb and Zn. Their present levels in the samples, alongside reference values from regulatory bodies are contained in Tables 1 and 2.

The amounts of the heavy metal contaminants in the water show significant variation ($P > 0.05$) between rainy and dry season, having subjected the data in Figure 1 to one way ANOVA. The result showed that the level of the contaminants was rather higher in the rainy season more than in the dry season, except for lead which was lower in the rainy season. This implies that the metal contaminants might have gained influx into the water body from the surrounding anthropogenic activities and from the deposits along the water flow, down to the studied area [23].

With respect to the WHO/SON permissible limit; Cd, Cu and Zn, all had concentrations within the acceptable limit during the rainy season. Where, Cr, Fe, Mn and Pb, had amounts above the limit [24]. Aside the inflow of these metals from the surrounding, iron easily get reduced from ferric (Fe^{3+}) to ferrous (Fe^{2+}) iron, in the presence of organic matter and as a result, producing more soluble iron [20].

Table 1. *Observed Amounts in mg/L of the Heavy Metals in Water at the Different Sampling Points in River Pil-gani in the Dry and Rainy Season.*

Sample location	Cd	Cr	Cu	Fe	Mn	Pb	Zn
Rainy Season Water Sample							
Angwang Tabo	0.0023 (0.0014)	1.9100 (0.0200)[a]	0.0031 (0.0016)[a]	0.0035 (0.0015)[a]	0.0623 (0.0075)[a]	0.0107 (0.0031)[a]	0.0024 (0.0017)[a]
Gongani	0.0023 (0.0015)	1.9633 (0.6716)[a]	0.0023 (0.0015)[a]	0.0030 (0.0017)[a]	0.0640 (0.0115)[a]	0.0063 (0.0025)[a]	0.0023 (0.0015)[a]
Pishe	0.0020 (0.0010)	1.9833 (0.4150)[a]	0.0033 (0.0015)[a]	0.8817 (0.0247)[b]	0.078 (0.0155)[a]	0.0079 (0.0030)[a]	0.0022 (0.0009)[a]
Zamadede	0.002 (0.0008)	1.7267 (0.2259)[a]	0.0025 (0.0005)[a]	0.0042 (0.0018)[a]	0.4767 (0.0851)[b]	0.0104 (0.0126)[a]	0.0023 (0.0006)[a]
Dry Season Water Samples							
Angwang Tabo	ND	ND[b]	ND[b]	ND[c]	0.0450 (0.0060)[a]	0.5973 (0.0425)[b]	ND[a]
Gongani	ND	0.07033 (0.0117)[b]	ND[b]	ND[c]	0.0650 (0.0151)[a]	0.9600 (0.0300)[c]	ND[a]
Pishe	0.0030 (0.0010)	0.4033 (0.0045)[b]	ND[b]	ND[c]	0.2937 (0.0470)[c]	0.5533 (0.0874)[b]	0.021 (0.0026)[b]
Zamadede	ND	ND[b]	ND[b]	ND[c]	0.0050 (0.0017)[a]	1.0967 (0.1050)[c]	ND
SON/WHO	0.003	0.050[b]	2.000[c]	0.300[d]	0.400[b]	0.010[a]	3.000[c]

Values are the mean (±standard deviation) of three replicate measures of the heavy metals at each sampling unit, except for the reference (SON/WHO).
Different alphabets on each column indicates significant difference ($p<0.05$)
ND = Not Detected.

Table 2. *Observed Amounts in mg/L of the Heavy Metals in Sediment at the Different Sampling Points in River Pil-gani in the Dry and Rainy Season.*

Sample location	Cd	Cr	Cu	Fe	Mn	Pb	Zn
Rainy Season Sediment Samples							
Angwang Tabo	1.9367 (0.0416)[a]	10.8033 (1.0900)[a]	5.1500 (0.2700)[a]	8349.3267 (2.5160)[a]	373.8300 (3.9275)[a]	0.0153 (0.0035)[a]	18.7000 (0.6183)[a]
Gongani	0.9303 (0.0095)[b]	17.8000 (0.7391)[b]	6.0500 (0.2883)[b]	33745.0000 (3.0512)[b]	287.04 (0.8008)[b]	0.0077 (0.0025)[a]	19.9003 (0.2560)[a]
Pishe	1.1900 (0.2476)[b]	20.8033 (1.0031)[b]	6.9300 (0.2008)[b]	36541.0000 (5.2915)[c]	287.0000 (0.8047)[b]	0.0107 (0.0015)[a]	18.2000 (0.2008)[a]
Zamadede	1.3200 (0.4073)[b]	15.0000 (1.8452)[b]	4.7600 (0.3005)[a]	91011.0000 (2.4000)[d]	271.0000 (0.7041)[c]	0.0033 (0.0040)[a]	19.1000 (0.3005)[a]
Dry Season Sediment Samples							
Angwang Tabo	7.3300 (0.6248)[c]	8.3800 (1.1650)[a]	8.4400 (0.1345)[c]	1744.0000 (6.0950)[e]	274.0000 (4.2720)[c]	256.0000 (5.9311)[b]	12.2000 (0.8602)[b]
Gongani	7.5400 (0.531)[c]	8.5500 (1.2857)[a]	10.4000 (1.0247)[d]	2254.9000 (4.6841)[f]	266.0000 (3.9661)[c]	277.0000 (6.6189)[c]	19.4000 (1.4030)[a]
Pishe	3.2200 (0.5444)[a]	5.1100 (1.3672)[c]	9.4400 (0.5556)[c]	2318.0000 (0.9502)[g]	321.0000 (1.7504)[d]	275.0000 (1.7840)[c]	22.6000 (0.7134)[c]
Zamadede	2.3400[c] (0.4251)	4.7300 (0.305)[c]	10.5000 (0.4784)[d]	2219.0000 (0.95394)[h]	341.0000 (1.1862)[e]	265.0000 (1.2507)[d]	21.3000 (0.5251)[c]
NOAA/WHO	4.9000[d]	26.0000[d]	25.0000[e]	2.0000[i]	300.0000[f]	35.8000[e]	120.0000[d]

Values are the mean (± standard deviation) of three replicate measures of the heavy metals at each sampling unit, except for the reference (NOAA/WHO).
Different alphabets on each column indicates significant difference ($p<0.05$)
ND Not Detected.

The levels of contamination of the examined heavy metals in the different sampling points in the rainy season show no significant variation. Significant variations were however, observed between Pishe and the rest of the sampling units, as well as Zamadede and the rest for Fe and Mn respectively. Copper and Iron were below detection in all the sampling units; Cd and Zn were detected only at Pishe. Traces amount of Mn were detected at all the sampling units but were within the acceptable limits. Also, Cr was observed at Gongani and Pishe, with all the concentrations higher than the permissible limit [24]. For Pb, the contamination levels were quite alarming as were reasonably above the acceptable limits [20, 24]. The general variations in the metal contents at different sampling points may be due to varying anthropogenic activities and metal deposit [23], alongside topology and sediment type found at the different sampling points [17].

On the other hand, the study of the levels of the contaminants in the river sediment for both seasons, significantly vary ($p<0.05$), having subjected the data to one way ANOVA. The observed levels of the contaminants are higher in rainy season with regards to; Cr, Mn and Zn. Meanwhile, Cd, Cu, Fe and Pb show higher concentrations in dry season, compared to rainy season. Heavy metals discharged into the water bodies are likely abstracted by sediment particles, leading to their accumulation in the sediment [2]. Sediment becomes bioavailability reservoir for the metals when the influx ceases [2]. This leads to their release through; chemical, biological and physical process occurring at the sediment-water interface and causing recontamination of the water [17].

The amount of cadmium was significantly lower than the threshold limit in all samples in rainy season, however, significantly higher concentrations were observed in Angwan Tabo and Gongani. Higher amounts were observed for chromium in all the sampling points, during the rainy season although, still within the acceptable limit as can be inferred from the baseline value set by the reference organizations [14, 24]. Copper on the other hand have higher content in the sediment in the dry season yet, the concentrations were still significantly lower than the threshold for safe sediment. Iron however, had dramatic high contents in the different sapling units of the study area and the values were way above the safety threshold for Fe content in sediment [14]. In the case of Mn, the concentrations in Angwan tabo during rainy season; Pishe and Zamadede during dry season were higher than the acceptable limit. Whereas, for the other sampling units; the concentrations of manganese in the sediment were within safety threshold. Lead has shown uniquely low concentrations in the sediment during the rainy season, the values were quit lower with regards to acceptable limit. Although, exceptional high amounts; ways above the permissible limit were recorded in all the sampling points [14, 24]. Variation in scavenging capacity of the sediment soil types and the anthropogenic activities in the different seasons may be responsible for the variation in the contaminants levels in the sediment [17].

4. Conclusion

From the foregoing, River Pilgani is generally not safe for domestic consumption as toxic metals are present in the river water at concentrations above the acceptable consumable levels. More also, there is tendency for recontamination of the water, through sediment-to-water metal transfer, giving that the sediment metal concentration is also above the permissible limits. It can also be agreed that the metals gain influx into the river as they are washed in from the river surrounding. This implies the need to assess the anthropogenic activities surrounding the river, having observed the presence of potential metal discharge sources. Pil-gani River is polluted with Pb, Cr and Fe, at varying degrees based on locations. Hence, the river water is not recommended for drinking, not even some domestic uses. In addition, the potential of recontamination of the water system is seeing to exist in Fe, Pb, Cd, and Mn; as the concentrations were above the permissible limit for sediment in some of the sampling units. The river water therefore, remains unsafe, unless and until identification of heavy metal originating source, control and remediation are carried out.

5. Recommendations

1. It is recommended therefore that, urgent attention of the surrounding community, Government and other concerned organizations and individuals be drawn to this fact, requiring immediate decease from consumption particularly drinking until and unless urgent address is made to the contamination/pollution of river Pil-gani.
2. Further elaborate studies should be carried out on the river Pil-gani to ascertain the true and extent of potential harm posed to humans and even plants irrigated therefrom, to the depth of detail sampling and analysis and to the width of wider heavy metal array and possibly other pollutants such as of organic class.
3. The river is not profiled in term of the heavy metals contamination at its entire length hence, requesting other communities along the river to take reference from the result of this studies to do elaborate and more detailed analysis of their tract sections of the river before freely utilizing the water.
4. Further recommendation is made to those living with similar anthropogenic activities around their consumable waters to assess them recurrently to avoid poisoning before taking precaution in event of risen levels of the toxic heavy metals and other pollutants.

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