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Assessment of Heavy Metals in Sediment of River Pil-Gani Plateau State Nigeria

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Abstract
River Pil-gany is exposed to natural and anthropogenic sources of heavy metals, which may pollute it causing toxicity to the dependent population and aquatic organisms. Sediment, an important part of water bodies, serves as reservoir/sink or secondary source of heavy metals, liable to re-contaminate the water hence, requires adequate monitoring attention. Heavy metals presence in the sediment was ascertained using Atomic Absorption Spectrophotometry while, contamination factor, pollution load index and geo-accumulation index were employed to assess the degree of contamination. Sediments from four sampling points were analyzed for selected heavy metals in rainy and dry seasons and were found to range thus; Cd (1.190 to 7.540), Cr (4.730 to 20.803), Cu (4.760 to 10.500), Fe (1744.000 to 8349.327), Mn (266.000 to 373.830), Pb (0.003 to 277.000), Zn (12.200 to 19.900) in mg/L respectively. The result of the aforementioned indices for the respective metals; Cd, Cr, Cu, Fe, Mn, Pb and Zn, for contamination factor index was in the ranges of (1.86 to 15.08), (0.06 to 0.28), (0.12 to 0.26), (0.05 to 2.52), (0.39 to 0.53), (0.00 to 17.31) and (0.19 to 0.35) respectively. Meanwhile for geo-accumulation, the ranges were (0.31 to 3.33), (-5.74 to -1.23), (-3.66 to -2.24), (-5.16 to -0.67), (-1.94 to -1.45), (-10.97 to 3.53) and (-2.94 to -2.12) respectively. The pollution load index for the study area was in the range (0.06 to 0.66). R**iver** Pil-gany sediment is moderately to highly contaminated due to the impact of anthropogenic activities thus requires frequent monitoring.
Keywords: Sediment, Heavy Metals, Pollution and Atomic Absorption Spectrophotometry.

Introduction

Heavy metals contamination of the aquatic system has become a major environmental challenge, in that all forms of life depend on quality water for existence [1]. Heavy metals are metals and metalloid elements that have specific density above 5 g/cm³, and relative atomic weight of 40.04 and above. 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. Heavy metals are a threatening class of pollutants because of their non-degradability, bioaccumulation, toxicity and persistence in the environment [2]. River Pil-gany water has found great use in various ways, which include; human consumption, farming, recreation and as habitat to several aquatic organisms. This further underscores the importance of assessing the quality of the water body and protecting it against contaminant sources.

Water contamination and pollution resulting from leaching of natural element deposits and man's interferences have greatly threatened the quality of water; to a point that despite the abundance of water, its availability for use is challenged [3]. Some of these metals are micronutrients to plants and animals, but at higher concentrations, they are toxic [4]. The degree of toxicity depends on the kind of metal and its chemical composition. For some of the metals, the most dangerous forms are those coupled to organic moieties. This is because they are soluble in animal tissues and can pass through biological membranes. Even in humans, toxicity effects are endless as seeing in attack on the central nervous system, leading to mental disorder, lungs, kidney, liver, blood composition and other important organs, causing life threatening damages [5].

Natural and anthropogenic activities are causes of heavy metals contamination however, majorly is anthropogenic activities [3]. Following these activities, heavy metals gain entrance into the aquatic ecosystem and are fractionated between the liquid phase and sediment during the transportation [6]. Sediment, which is an ultimate sink for heavy metals discharged into the aquatic system [1], receives a major fraction of the heavy metals which eventually get accumulated within, leaving a small fraction to stay dissolved in the water [6]. Heavy metals enrichment of sediment depends on the following; pH, grain size, organic matter, cation exchange capacity and hydraulic conductivity [1]. Sediment, the main reservoir of entry and precipitated heavy metals is regarded as one of the most important components of the aquatic system; as it has longer duration of stay, more especially for flowing water bodies [6]. More also, when heavy metals balance in the liquid phase collapses, the sediment releases back the heavy metals through ion-exchange, desorption, and dissolution processes to recontaminate the water [7].

Therefore, sediment quality has become an important indicator of pollution in water [1]. Sediment is regarded as the most appropriate indicator to be monitored in environmental evaluations and to understand their potential risk factor due to the ecological importance and the persistence of heavy metal pollutants in aquatic ecosystem [1]. Many literature works have agreed that in aquatic ecosystem, sediment has been employed as environmental indicator, where their chemical analysis provides important and sufficing information on the impact of anthropogenic activities on contamination and pollution levels [8, 9].

In recent decades, different sediment metal pollution indices have been developed and applied to water environment, to evaluate the degree to which sediment-associated chemical status might adversely affect aquatic organisms [1, 6]. Famous among these indices include; enrichment factor (EF), metal enrichment index (MEI), geo-accumulation index (Igeo), contamination factor (CF) and pollution load index (PLI) [6]. Reference values of these parameters are used to screen the potential for contaminants within sediment to induce biological effects and to compare sediment contaminant concentration with the corresponding quality guideline [1, 10]. One of the most commonly used pollution index is the enrichment factor (EF); it determines whether sediment resident metals are naturally (from rocks) or anthropogenic sources [11]. Contamination Factor (CF) is used to evaluates the enrichment of metals based on the background concentrations of each metal in sediments [1]. Also, Geo-accumulation Index (Igeo) is a frequently used index to evaluate the degree of anthropogenic and geogenic accumulated pollution loads [1, 12]. It is reported with great success in heavy metal accumulation especially in the sediment due to industrial activity [12-13]. Pollution load index simply describes the magnitude of heavy metal pollution in sediment [14]. The value classifications for the various indices are provided in Table 1 below. This research therefore, seeks to evaluate the degree of pollution of River Pil-gani sediment.

Table 1: Indices for Sediment Heavy Metal Quality Classification

Parameters	Quality classification	References
CF	CF<1 = low contamination	[15]
	1≤CF<3 = moderate contamination	
	3≤CF<6 = considerable contamination	
	CF≥6 = high contamination	
Igeo	Igeo≤0 = practically uncontaminated	[16]
	0<Igeo<1 = uncontaminated to moderately contaminated	
	1<Igeo<2 = moderately contaminated	
	2<Igeo<3 = moderately to strongly contaminated	
	3<Igeo<4 = strongly contaminated	
	4<Igeo<5 = strongly to extremely contaminated	
	Igeo≥5 = extremely contaminated	
PLI	PLI <1 no pollution	[14]
	PLI is >1 deterioration	

Materials and Methods

Materials

Reagents and Apparatus

All reagents used in this work were of analytical grade. They include $FeSO_4.7H_2O$ (purity of 96 %; model No. 28400) and other common chemicals like HNO_3, HCl and H_2O_2.

Apparatus used in the study include; Hot Plate 220 v/450 w Digital Weighing Metre (EM-HP1000S SKU122755461), Horiba water Quality Monitor (Model: U-500) and Flame Atomic Absorption Spectroscopy (Varian Spectra AA).

Methods

Sampling

Sediment samples were collected at four points, at about 2-3 km intervals along River Pil-gani, Kafel Langtang North Metropolitan area, as shown in Figure 1. The sampling points include; Angwan tabo, Gwongani, Pishe and Zamadede. Human settlements, industrial activities such as;

fiber making, smelting, brewing, brick making and confectionary, the Naraguta leather industry and tin mine site are all resident around the study area. Alongside the aforementioned are agricultural activities, medical facilities, waste dump sites and effluents from waste water treatment as well as metal deposits such as lead and limestone; all of which pose great potential for heavy metals pollution.

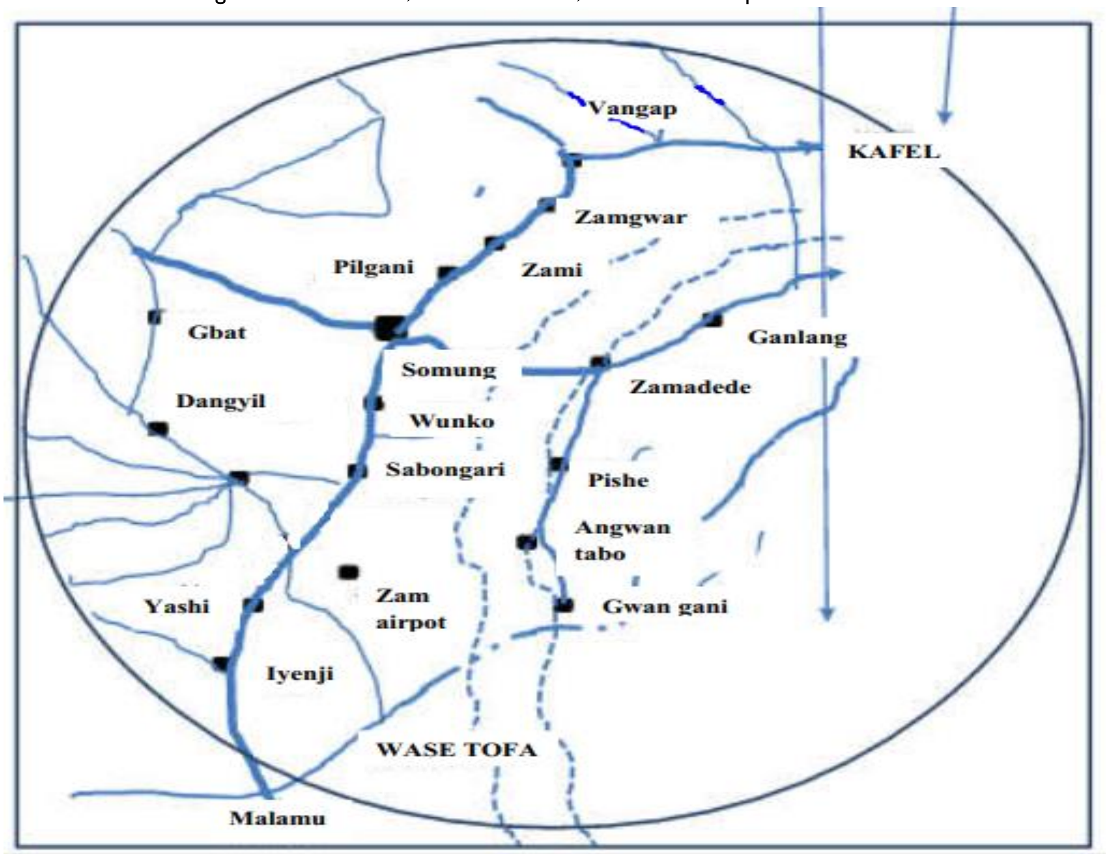

Figure 1: Map of the Study Area [17]

Collection and preparation of sediment samples
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

Sediment pollution indices

(a) Enrichment Factor (EF) is defined as a factor used in assessment of the degree of contamination with heavy metal. Equation (1) below represents the EF

$$EF = (\frac{C/Fe\ (sample)}{(C/Fe(earth\ crust)} \qquad (1)$$

Where C/Fe (sample) is the content of the examined and the reference element in the examined locations, C/Fe (earth crust) is the content of the examined and reference element in the reference environment (World Surface Rock Average) (WSRA).

(b) Contamination Factor (CF) gives an indication of the degree of contamination of heavy metals in the soil. The level of contamination factor of sediment by metal is expressed in equation 2.

$$CF = \frac{(C-Sample\ )}{C-\ Background)} \qquad (2)$$

Where C-Sample is the given metal in the sediment, C-Background is the background value of the metal. The C-Background value equals to the world surface rock average.

(c) Geo-accumulation index (I_{geo}) determines the concentration of metal accumulation in sediment above the baseline concentration. It is expressed as shown in equation 3.

$$Igeo = log_2[\frac{Cn}{Bn1.5}] \qquad (3)$$

Where Cn is the measured concentration of the element ‘n’and Bn is the geochemical background value. In this study, Bn = world surface rock average given. The factor 1.5 is incorporated in the relationship to account for possible variation in background data due to lithogenic effect.

(d) Pollution Load Index (PLI) is used in evaluating the pollution level in an environment. The mathematical expression is represented by equation 4.

$$PLI = CF_1 \times CF_2 \times CF_3 \times \dots CF_n)^{\frac{1}{n}} \qquad (4)$$

Where, CF is the contamination factor and n is the number of metals investigated (seven in this study).

Statistical analysis

The values of the heavy metals concentrations were subjected to statistical analysis, using Statistical Package for Social Sciences version 20.0. One way analysis, conducted at 95 % confidence level and multiple comparisons (Tukey post hoc test) were used to ascertain the levels of variations within the metals in the different sampling points and the seasons.

Results and Discussion

Table 4: Mean Heavy Metals Concentrations in River Pil-gani Sediment

Sample location	Cd (mg/L)	Cr (mg/L)	Cu (mg/L)	Fe (mg/L)	Mn (mg/L)	Pb (mg/L)	Zn (mg/L)
Rainy Season Sediment Samples							
Angwang Tabo	1.94 ± 0.04^{a}	10.8 ± 1.09^{a}	5.15 ± 0.27^{a}	8350 ± 2.52^{a}	374 ± 3.93^{a}	0.015 ± 0.00^{a}	18.7 ± 0.62^{a}
Gongani	0.93 ± 0.01^{b}	17.8 ± 0.74^{b}	6.05 ± 0.29^{b}	33750 ± 3.05^{b}	287 ± 0.80^{b}	0.0077 ± 0.00^{a}	19.9 ± 0.26^{a}
Pishe	1.19 ± 0.25^{b}	20.8 ± 1.00^{b}	6.93 ± 0.20^{b}	36541 ± 5.29^{c}	287 ± 0.81^{b}	0.011 ± 0.00^{a}	18.2 ± 0.20^{a}
Zamadede	1.32 ± 0.41^{b}	15.0 ± 1.85^{b}	4.76 ± 0.30^{a}	91011 ± 2.40^{d}	271 ± 0.70^{c}	0.0033 ± 0.00^{a}	19.1 ± 0.30^{a}
Dry Season Sediment Samples							
Angwang Tabo	7.33 ± 0.63^{c}	8.38 ± 1.17^{a}	8.44 ± 0.15^{c}	1744 ± 6.10^{e}	274 ± 4.27^{c}	256 ± 5.93^{b}	12.2 ± 0.86^{b}
Gongani	7.54 ± 0.53^{c}	8.55 ± 1.29^{a}	10.4 ± 1.03^{d}	2255 ± 4.68^{f}	266 ± 3.97^{c}	277 ± 6.62^{c}	19.4 ± 1.40^{a}
Pishe	3.22 ± 0.54^{a}	5.11 ± 1.37^{c}	9.44 ± 0.56^{c}	2318 ± 0.95^{g}	321 ± 1.75^{d}	275 ± 1.78^{c}	22.6 ± 0.71^{c}
Zamadede	2.34 ± 0.43^{c}	4.73 ± 0.31^{c}	10.5 ± 0.48^{d}	2219 ± 0.95^{h}	341 ± 1.19^{e}	265 ± 1.25^{d}	21.3 ± 0.53^{c}
NOAA/WHO	4.90^{d}	26.0^{d}	25.0^{e}	2.00^{i}	300^{f}	35.8^{e}	120^{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 indicate significant difference ($p<0.05$)

Table 5: River Pil-gani Sediment Heavy Metals Pollution Indices

Sample location / Contaminants/ Parameters		Angwang Tabo		Gongani		Pishe		Zamadede	
		Rainy season	Dry season	Rainy season	Dry season	Rainy season	Dry season	Rainy season	Dry season
Cd	CF	3.88	14.7	1.86	15.1	2.38	6.44	2.64	4.68
	Igeo	1.37	3.29	0.31	3.33	0.67	2.10	0.82	1.65
Cr	CF	0.15	0.11	0.24	0.12	0.28	0.07	0.20	0.06
	Igeo	-3.37	-3.64	-2.64	-3.64	-5.74	-4.32	-2.89	-1.23
Cu	CF	0.13	0.21	0.15	0.26	0.17	0.24	0.12	0.26
	Igeo	-3.54	-2.24	-3.31	-2.56	-3.11	-2.64	-3.66	-2.47
Fe	CF	0.23	0.05	0.92	0.06	1.02	0.06	2.52	0.06
	Igeo	-2.69	-5.16	-0.67	-4.64	-0.67	-4.64	0.76	-4.64
Mn	CF	0.53	0.40	0.42	0.39	0.42	0.47	0.40	0.50
	Igeo	-1.45	-1.89	-1.83	-1.94	-1.83	-1.64	-1.91	-1.60
Pb	CF	0.00	16.00	0.00	17.31	0.00	17.19	0.00	16.56
	Igeo	-11.0	3.41	-11.0	3.53	-11.0	3.52	-10.8	3.46
Zn	CF	0.29	0.19	0.31	0.30	0.28	0.35	0.29	0.33
	Igeo	-2.38	-2.94	-2.93	-2.32	-2.42	-2.12	-2.35	-2.18
PLI: (Cd.Cr.Cu.Fe.Mn.Pb.Zn)		0.10	0.58	0.10	0.66	0.06	0.56	0.08	0.53

The concentration of the heavy metals in the river sediment viz. Cd, Cr, Cu, Fe, Mn, Pb and Zn is presented in Table 4. Meanwhile, Sediment contamination assessment for cadmium in respect of contamination factor, geo-accumulation index and pollution load index are presented in Table 5.

The amount of Cd in the sediment was higher in dry season compared to rainy season, implying it was not freshly washed into the river. This further indicates that there is tendency for recontamination of the water body from the sediment which now acts as a secondary source of Cd [6]. Despite anthropogenic activities like unsafe use and handling of Ni–Cd batteries, industrial activities, waste treatment plant, as well as agricultural fertilizer, Cd exist naturally in soil rocks [18]. Nature may be the possible source of contamination through dissolution. Following the WHO threshold, the concentration in all instances is within acceptable limits of 4.900 mg/L, except for Angwan

Tabo and Gongoni in dry season [19]. Cd being a non-essential element is known to cause renal dysfunction, bone degeneration, liver and blood damage on exposure [20]. It also has highest soil to plant mobility than any other metal. Contamination factor values of Cd showed that, the degree of contamination of the observed data run from moderate to high contamination [16]. For the rainy season, all sampling points fell within the moderate contamination except, Angwan Tabo, which had values within considerable contamination range. For the dry season records, all the values of the index were within the high contamination range except for Zamaded which was within the considerable contamination range. The contamination based on geo-accumulation of Cd showed that in the case of rainy season, all the sampling points were moderately contaminated. Dry season records show that Angwan Tabo and Gongoni were strongly contaminated while the rest of the sampling points were moderately contaminated [17]. The contamination recorded may be from influx of metals discharged from the industries resident within the locality of the studied water body [1].

Chromium however, appeared to be more concentrated in rainy season than in the dry season. This may be that a certain amount must have dissolved into the liquid phase or was washed away. The pattern is similar to that reported by Eka *et al*. [21] In the case of chromium; all the recorded concentrations were below the set limit of tolerance of 26.000 mg/L by NOAA/WHO [19]. More also, hexavalent chromium is more toxic than trivalent chromium, hence, its impact depends on the chemical form in which it exists in. The contamination factor index values of Cr for all the sample points, and the seasons were within range of low contamination [16]. The geo-accumulation index values of less than zero imply practical uncontamination [17]. This further implies that the presence of the chromium may likely be natural and less anthropogenic.

Copper concentration in the sediment was higher in dry season than in the rainy season, indicating that it was not freshly washed in; it could be from deposits of previous contamination which dissolved as the seasons changed [1]. Similar result was obtained in the study carried out by [21] in which the industrial activities within the study area were said to be the cause. As established by NOAA/WHO [19], the acceptable limit of concentration for Cu in sediment of 25.000 mg/L was not exceeded, implying the sediment is within safety range. The observed concentration implies no tendency for copper related health complications like brain damage, demyelization, renal disease and copper deposition in the cornea and even death [22]. The recorded contamination factor index values of copper in the four sampling points in both the rainy and dry seasons, all fall within the low contamination range [16]. Also, the geo-accumulation index values for all the seasons were within the practically uncontaminated rage [17].

Iron being an essential element and an element in great abundance; the excessive presence in the sediment particularly during the rainy season which possibly is through washing in is not out of place. However, even essential metals, in higher concentrations are toxic to man and other living organisms. In all the sampling units and seasons, the concentration of was way above the permissible limit of 2.000 mg/L [19]. Iron contamination factor index values for the four sampling units for the rainy and dry seasons were within the low contamination range, exception of Pishe and Zamadede which had values within moderate contamination in the rainy season [16]. The geo-accumulation index on the other hand had values implying the sampling points were practically uncontaminated for both the rainy and dry seasons, exception of Zamadede during the rainy season which fell within uncontaminated to moderately contaminated range [17].

Manganese had no clear pattern of concentration variation although; its concentration was slightly more in dry season. In the rainy season only Angwan Tabo that had Mn concentration above the threshold value of 300.00 mg/L [19]. In the dry season, both Pishe and Zamaded had concentrations above the permissible limit. The degree of contamination based on contamination factor index for Manganese as observed in the study show that, for all the sampling units and seasons, the values imply low contamination [16]. Similarly, the geo-accumulation index values agreed that the study area was pract 24 uncontaminated [17].

Lead had a clear pattern of exceptionally high content in dry season, compared to rainy season. This indicates that the industries within the area caused a great influx which became adsorbed as the water dried up. Similar pattern has been reported by [21] in the study "Sediment Quality Assessment by Using Geochemical Index at Saguling Reservoir West Java Province Indonesia". The observed concentrations in the rainy season were all below the permissible threshold limit of 35.800 mg/L [19]. However, the dry season concentration was seeing to be way above the set limit. Should this exceptionally high lead content translate to availability in the liquid phase, a case of lead poisoning may arise, a similar fate of Shikira area of Niger State and Zamfara [1]. Toxicity level of lead is so high that even at low concentration; it can pose significant threat to the ecosystem [23]. Based on contamination factor index, all the sampling units were within low contamination range in the rainy season. However, in the dry season all the sampling units were highly contaminated [16]. The degree of contamination is further confirmed by the geo-accumulation index values which agree that the study area was practically uncontaminated in the rainy season but extremely contaminated in the dry season [17].

Zinc also, had on average higher concentration in the dry season compared to rainy season, even though, still within close range. This observed concentration can be attributed to influx from environment during the rainy season which has been adsorbed and concentrated as the water dries. However, in all instances, the concentrations were within the limit of acceptance as they were way below the threshold [19]. The assessment of the degree of contamination of zinc based on contamination factor index implied that the all the sampling units in the study area in both the rainy and dry seasons were lowly contaminated except [16]. Similarly, the prediction of contamination factor index is confirmed by geo-accumulation which agreed that the study area was practically uncontaminated for all the sampling units and in both seasons [17].

The estimated pollution load index for the monitored metals in the studied area for all the sampling units was less than 1, implying no pollution [14].

Conclusion

From the foregoing, it can be agreed that the sediment from River Pilgani is moderately to highly contaminate as characterized by the quality indices. Even though not polluted, potential threat of water pollution through recontamination still exists. Furthermore, the results of the contamination indices imply that anthropogenic activities have contributed. Hence, it is therefore pertinent to continue monitoring the contamination levels and further extensive studies should be carried out on the water and sediment to avoid the instances of heavy metal poisoning. This also should serve as a reminder to the need for more stringent sanitation policies and compliance to curtail careless discharge of effluents and waste generally. Lastly, the water and sediment quality status of this river should awaken the need to monitor like-bodies of water for humans and environmental safety**.**

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