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Risk Assessment of the Impact of Oil Spill on the Heavy Metal Content of Santa Barbara River in Bayelsa State, Nigeria

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Abstract

This study was aimed at assessing both the effect (risk) and impact of a recent oil spill on heavy metal concentration in the Santa Babara River in Bayelsa State, Nigeria. Samples were collected and preserved based on standard methods. The heavy metals of interest were Mercury (Hg), Arsenic (As), Cadmium (Cd), Chromium (Cr) and Copper (Cu) due to their levels of toxicities and presence in water bodies while the five study stations were Worokuma (W), Uwanga (W), Tuweni (T), Shellikiri (S), Inarakiri (I) and Esenfakiri (E). The solar thermos elemental flame atomic absorption spectrometer (AAS), model SE-71096 made in Germany with detection limit of 0.001 mg $\cdot kg^{-1}$ was used for the heavy metal analysis. The trend of heavy metal abundance was found in this order Cr>Cu>Cd>Pb>Hg=As. All the detectable metals had risk index of greater than 5 but the highest was found in the order, Cd> Pb > Cu > Cr (149, 35, 26 and 12 respectively) which meant extremely high level of pollution. This also indicated the probability of non-carcinogenic effects occurring and increases as HI increases signifying carcinogenic risk via direct ingestion of water. Graphs were used to show trends in both mean heavy metal concentrations and risk assessment indices. Chromium and Pb had moderate contaminations for CF and CDI values, hence regular monitoring of the Santa Barbara River is of essence as most of the inhabitants take this as the only source of potable water as their wells have very high iron content.

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INTRODUCTION

Oil spills usually contain a lot of organic and inorganic materials which may contaminate water bodies both ground and surface water, amongst these are the heavy metals such as arsenic, lead, cadmium, mercury, copper, chromium *etc*. These may be based on the production additives but heavy metals are considerably toxic, have densities usually above 5g/cm^3 and Heavy can also be defined as metals with densities that are five times higher than water (Emmanuel *et al*., 2018; Iyama *et al*., 2022). Heavy metal pollution of rivers, lakes, fish and sediments have become a major environmental focus recently because they are one of the most serious pollutants in our natural environment due to their toxicity and persistence (Gborade, 2013). In the aquatic environment, trace elements are distributed amongst the various environmental components such as water, suspended solids, sediments and biota (Shakweer & Abbas, 2005).The physicochemical properties of crude oil spills vary considerably depending on the geographic location of the field, the geologic formation, and the type of hydrocarbon product being produced (Ekins *et al*., 2007; Bakke *et al*., 2013; Gazali *et al*., 2017). Dispersed oil, aromatic hydrocarbons and alkylphenols (AP), heavy metals, and naturally occurring radioactive material (NORM) are of particular environmental concern because the water has been in contact with hydrocarbon-bearing formations (Neffe *et al*., 2011; Bakke *et al*., 2013).

Heavy metals are generally elements whose densities are comparatively high, toxic even at low concentrations and recalcitrant as environmental contaminants (Lenntech, 2004; UNEP, 2004). They are regularly introduced into water bodies through rivers, runoff, and land-based point sources where metals are produced in anthropogenic industrial activities (Bazrafshana, 2015). Heavy metal contamination remains an environmental challenge in both underdeveloped and developed countries (Zhang *et al*., 2007; Lee *et al*., 1990). Certain environmental conditions may lead to ecological damages due to toxic levels of heavy metal accumulations (Jefferies & Freestone, 1984; Bonnett, 1989). Environmental pollution due to oil spillages had become a challenge and topical in world public health issues as industrial effluents such as oil spills are sources of contamination to land, swamps, rivers, estuaries and coastal waters (Olu *et al*., 2019). Such anthropogenic pollutants were the main sources of heavy metal contaminants in aquatic environment (Gibbs & Miskiewics, 1995). Water is a vital component of life as fresh water accounts for about 3% of the total water on the earth surface, and only 0.01% of this fresh water is available (Amini *et al*., 2016; Moghaddama *et al*., 2018).

Water pollution occurs when unwanted materials (with potentials to threaten human and other natural systems) find their way into rivers, lakes, wells, streams, boreholes or even reserved fresh water in homes and industries (Aboyeji, 2013). Heavy metals in water may be natural (weathering of rocks and soils) and anthropogenic (mining, industries, wastewater irrigation and agricultural activities (Chanpiwat *et al*., 2010; Muhammad *et al*., 2010). Large quantities of heavy metals have been released into rivers worldwide due to global rapid population growth and anthropogenic activities (Srebotnjak *et al*., 2012; Su *et al*., 2013; Islam *et al*., 2014; Islam *et al*., 2015).

The ecology all over the biosphere has been greatly changed due to the influence of human activities which has led to the contamination and pollution of the environment and increased loss of biodiversity (Raven, 2002; Li & Yang, 2008). Heavy metal concentrations generated from anthropogenic sources (including Cd, As, Pb, Cu, Fe, Zn, Mn, and Cr) to coastal environment can cause a potential risk to the natural environment (Emmanuel *et al*., 2018). The use of this river as drinking water source is a major challenge as no other sources hence is hazardous to human health, crops, fish and soils if not treated before use especially for (Moslen *et al*., 2018).

There was an oil spill into the tidal Santa Barbara River which is fresh water by the wet season but saltwater by the dry season and a major source of drinking water for over fifty (50) fishing settlements. This spill was of serious concern as reported by various environmental organizations. "Aiteo Eastern Exploration and Production Company (AEEPCO), Operator of the NNPC /Aiteo Joint Venture of Oil Mining Lease (OML) 29 on Friday, 5 November 2021, reported a hydrocarbon well head leak in its Santa Barbara, Southwest field, in Nembe Local Government Area of Bayelsa State," the company said in a statement on November 22. The spill occurred in a form of fountain within the proximity of Opu Nembe Community at Well 1, Wellhead located at the Southern Field of Santa Barbara". This oil spill has caused a lot of fish kills and mangrove devastation as is

visually noticed. The water is no safer for drinking by the natives but of great concern is the heavy metal input which has so many environmental and public health concerns. The aim of this study is to assess the risk of the impact of oil spill from Santa Barbara oil rig location on the heavy metal content of Santa Barbara River in Bayelsa State, Nigeria and compare with safety standards. This will be further buttressed using risk assessment models to ascertain the level of safety.

METHOD

Materials and Methods

Santa Barbara oil rig also known as OML 29 or Santa Barbara flow Station (OML 29) is an onshore oil production platform located in Santa Barbara River, South of Brass Creek and East of Odiama Creek in Nembe local government Area of Bayelsa State, Nigeria. It is owned by Nigerian National Petroleum Corporation (NNPC) and AITEO Energy Resources. Its geographical coordinates are Latitude 4.3358,40 20. 89" North and Longitude 6.6022, 60 36.81" East. The sampled communities are shown in Table 1 and Figure 2 below.

Table 1. Sampled communities and their geographical locations

Community/ Location	Geographical Co-ordinates	Description of Prevalent Activities
1.Worokuma(W)	4.50989 (N 4^0 30'35.93''), 6.55802 (E 6^0 33'28.85'')	Fishing expedition and sales of drinks and petroleum products
2.Uwanga (U)	4.48638 (N 4^0 29'10.95''), 6.58862 (E 6^0 35'19.044'')	A fishing and periwinkle picking settlement community
3.Tweni 1 and 2 (T)	4.48592 (N $4^0$29'9.61''), 6.57536 (E 6^0 34'30.74'')	A relatively large settlement where government medical intervention team was met. Sales of petroleum products to boat operators, inhabitants and provision stores
4.Shellikiri (S)	5.53311(T 4^0 31'59.69''), 6.53982 (E 6^0 32'13.70'')	No inhabitants but called Juju point and a visible oil pipeline
5. Inarakiri (I)	4.53215 (4^0 31'55.86''), 6.55118 (E $6^0$33'4.36'')	Fishing settlement
6.Esenfakiri (E)	4.53538 (4^0 32'7.374''), 6.49874 (E $6^0$29'50.01'')	Sales of petroleum products, drinks and beverages
7. Nembe Town (N) Jetty	4.53825 (4^0 32'17.25''), 6.40712 (E $6^0$24'25.996'')	No impactful activities except being an assembly point for commuters

Source: Field Survey (2022)

Figure 1. Map of the Study Area (Source: Study Survey)

Sampling and Sample Collection

Collection of water samples from Santa Barbara adjoining communities of flow Station (OML 29) was done using sterilized plastic bottles whose content is fixed using 4.5 mils/l HNO_3. Water samples were collected from jetties of frontline communities of Worokuma (W), Uwanga (W), Tuweni (T), Shellikiri (S), Inarakiri (I), Esenfakiri (E) upstream, downstream and from a control point (land area wells) of Santa Barbara River. The upstream samples were

collected 1km from the Jetty points while the downstream water samples were collected 1km apart (in between). The sampling stations were selected based on their proximity to effluent discharge points (AITEO Well Head) in which water samples were used as point sources of pollution along the river, while wells were sampled as control. In the field, the containers were severally rinsed with habitat water at each sampling point prior to collection. Each sample was collected by submerging the receiving container into the river at about 100 mm to 200 mm below the surface with the open end aligned against the flow direction of water current. Immediately after collection of each sample, sample containers were appropriately labelled and immediately stored in an ice packed cooler box. The samples were thereafter transported to the laboratory within 24 hours for processing and heavy metal analyses. Sample storage was done according to standard laboratory practices as recommended by the American Public Health Association (APHA, 1998). At the beginning of water sample collection, each plastic container was thoroughly washed using the Santa Barbara water to ensure quality control.

Heavy metal analysis was done using the solar thermos elemental flame atomic absorption spectrometer, model SE-71096 made in Germany with detection limit of 0.001 mg·kg^{-1} at Jaros Inspection Services Ltd., Iwofe Road, Port Harcourt, Nigeria. The AAS was fitted with specific lamp (hollow cathode lamp of the analyte) of a particular heavy metal, while the other conditions were the same.

Samples Collection and Analyses

Water samples were collected from the Santa Barbara River same period from one station to another but within a time space of 4.00 hours in December, 2022. The samples were collected with a 1 litre water sampler, transferred into a clean 250ml plastic bottle and acidified with Nitric acid (HNO_3). The water samples were digested using concentrated Analar Nitric acid (Zhang *et al.*, 2007).

Research and Sampling Designs

The pure experimental (experimental with control) and cross-sectional survey designs (samples were taken at different points in time) were adopted for the study.

Statistical Analysis

The mean, standard deviation, analysis of variance and t-test were used to determine the spatial relationships in the study stations and concentrations, as well as also for that between two different stations, respectively, at 95% confidence level ($p \leq 0.05$). All the results were statistically analysed using single factor ANOVA and Tukey HSD test was performed to determine the levels of significant differences (Ogbeibu, 2014). Similarly, different health risk assessment models and graphs were used to illustrate existing trends around the three campuses to ascertain the health implications.

Risk Assessment Models

1. Contamination Factor (CF)

The Contamination Factor (CF) is calculated using equation 2 and shows site specific contamination of toxic substances (Harikumar *et al.*, 2009).

$$CF = Cm(sample)/Cm(background) \quad (1)$$

Where; C_m (sample) =concentration of a given metal at a contaminated site; C_m (background) = concentration of a given element in a control or background sample. The CF is based on 4 categories: Low contamination (CF<1), moderate contamination (1≤CF<3), considerable contamination (3≥CF<6), very high contamination (CF>6) (Wang *et al.*, 2006). C_m (background) is the standard pre-industrial reference level (in mg/kg): 70 for Pb, 1.0 for Cd, 90 for Cr, 50 for Cu, 15.0 for As (Namaghi *et al.*, 2011; Nordberg *et al.*, 2001).

2. Pollution Load Index

The Pollution Load Index (PLI) was calculated using the formula in equation 2 (Tomlinson *et al.*, 1980)

$$PLI = (CF_1 \times CF_2 \times CF_3 \ldots CF_n)^{1/n} \quad (2)$$

CF =contamination factor, n= number of metals studied, C_{metal} =concentration of metal pollutant in water; $C_{background}$ =background value of the metal.

3. Ecological Risk Factor (E_rF)

The E_rF can be calculated using equations 3 (Hakanson, 1980).

$$ErF = TR\ CF \quad (3)$$

Where TR= toxic response factor and CF= contamination factor

Interpretations of E_rF is as follows; ErF<40 and RI<150-low risk; 40≤ErF<160 and 150≤RI<300-moderate risk; 80≤ErF<160, 300≤RI<600-considerable risk, 160≤ErF<320-high, ErF≥320 and RI≥600.

4. Chronic Daily Intake (CDI_{ing}) via ingestion:

The result could be obtained using eqn.4 below:

$$CDIing = Csoil * Ring * EF * \frac{ED}{BW} * AT * 10 - 6 \quad (4)$$

R= Rate of ingestion (100mg/day in adult and 200mg/day in children), EF=exposure frequency (350d/a), ED=exposure duration (24 yrs in adults and 6 yrs in children), BW= body weight of the exposed individual (70kg in adults, 15kg in children), AT= averaging time in days (365 × ED adult/ children) [Reference dose (R_fD) for metals are; Cu= 0.04, Pb=0.0035, Cd=0.001, Cr=0.0003].

5. Hazard Quotient (HQ)

HQ is ratio between exposure and the reference oral dose (RfD) as given in equation 5. If the HQ<1, no obvious risk but if HQ>1, then risk is obvious.

$$HQ = \frac{CDI}{RfD} \quad (5)$$

Where (Div) = daily intake of bitter leaf (kg per day), (Cmetal) = concentration of metal in the bitter leaf (mg kg-1), RfD is the oral reference dose for the metal (mg kg-1 of body weight per day), and Bo= human body mass (kg), RfD= estimate of a daily oral exposure for the human population which does not cause deleterious effects during a lifetime, generally used in EPA's non-cancer health assessments. Values of RfD for Cd (0.001 mg kg-1 per day), Ni (0.02 mg kg-1 per day) and Cr (1.5 mg kg-1 per day) were taken from Integrated Risk Information System [38] (US EPA, 2010). The value of RfD for Pb (0.0035 mg kg-1 per day) was taken from WHO [39] (1993) standards. The average Bo was taken as 70 kg for adults (WHO, 1993), and 19.25kg for children 0-6 years old (IBGE, 2006).

6. Hazard Index (HI)

The hazard index is the sum of the hazard quotients, as shown in equation 6. HI<1-no risk from non-carcinogenic effects; HI>1-adverse health effects possible and has probability of effects increasing with the increases in the HI value

$$HI = \sum HQ = HQFe + HQPb + HQCd + HQCr + HQNi \quad (6)$$

7. Carcinogenic Analysis (ILCR)

The incremental lifetime cancer risk (ILCR) is defined as the incremental probability of a person developing any type of cancer over a lifetime as a result of twenty-four hours per day exposure to a given daily amount of a carcinogenic element for seventy years (Grzetic & Ghariani, 2008). Equation 7 is commonly used for the calculation of the lifetime cancer risk.

$$ILCR=CDI.CSF \quad (7)$$

Where, CSF is the cancer slope factor and is defined as the risk generated by a lifetime average amount of one mg/kg/day of carcinogen chemical and is contaminant specific, CDI is the chronic daily intake. The permissible limits are considered to be 10^{-6} and $<10^{-4}$ for a single carcinogenic element and multi-element carcinogens (Tepanosyan *et al.*, 2017).

RESULT AND DISCUSSION

The results of the study are presented in Tables 2-6 below.

Table 2. Heavy Metal Content of Worokuma (W) Study Station

Heavy metals (mg/l)	Study Stations					Standards (WHO, mg/l)
	W_A	W_B	W_C	Control	Mean	
Hg	<0.001	<0.001	<0.001	<0.001	<0.001	0.006
Cd	0.106±0.006	0.107±0.005	0.129±0.011	0.128±0.010	0.114	0.003
As	<0.001	<0.001	<0.001	<0.001	<0.001	0.010
Cu	0.204±0.000	0.203±0.000	0.203±0.000	0.213±0.006	0.204	2.000
Pb	0.019±0.000	0.019±0.000	0.022±0.001	0.016±0.003	0.020	0.010
Cr	0.194±0.020	0.194±0.020	0.277±0.040	0.373±0.107	0.222	0.050

Source: Field Work (2021)

Table 2 showed that Hg in all the sampled stations recorded values below 0.001 mg/l. Station W recorded 0.106±0.006 (W_A), 0.107±0.005 (W_B), 0.129±0.011 (W_C) while the control station had 0.114mg/l for Cd and mean as 0.114 mg/l. Similar to Hg was As which were below 0.001mg/l in all the stations including the control. Copper (Cu) recorded 0.204±0.000 (W_A), 0.203±0.000 (W_B), 0.203±0.000 (W_C) and control as 0.213±0.006 while the mean was 0.204 mg/l. Lead (Pb) in stations W_A and W_B recorded concentrations of 0.019±0.000, while W_C had 0.022±0.001, control station had 0.016±0.003 as the mean was 0.020mg/l. The concentrations of Chromium (Cr) in the study were same in W_A and W_B as 0.194±0.020, while W_C was 0.277±0.040 and the control and mean were 0.373±0.107 and 0.222mg/l respectively.

Table 3. Heavy Metal Content of Uwanga (U) Study Station

	Study Stations					
Heavy metals	U_A	U_B	U_C	Control	Mean	Standards (WHO,mg/l)
Hg	<0.001	<0.001	<0.001	<0.001	<0.001	0.006
Cd	0.106±0.004	0.106±0.004	0.124±0.008	0.128±0.011	0.112	0.003
As	<0.001	<0.001	<0.001	<0.001	<0.001	0.010
Cu	0.174±0.010	0.170±0.008	0.134±0.018	0.213±0.038	0.159	2.000
Pb	0.013±0.001	0.014±0.002	0.005±0.004	0.016±0.004	0.011	0.010
Cr	0.241±0.001	0.242±0.002	0.233±0.004	0.373±0.095	0.239	0.050

Source: Field Work (2021)

Table 3 showed that Hg and As in all the sampled stations recorded values below 0.001 mg/l. Stations U_A and U_B for Cd recorded 0.106±0.004, 0.124±0.008 (U_C), 0.128±0.011 for control while the mean was 0.112 mg/l. Copper (Cu) recorded 0.174±0.010 (U_A), 0.170±0.008 (U_B), 0.134±0.018 (U_C) and control as 0.213±0.038 while the mean was 0.159 mg/l. Lead (Pb) in stations U_A and U_B recorded concentrations of 0.013±0.001 and 0.014±0.002, while U_C had 0.005±0.004, control station had 0.016±0.004 with the mean as 0.011 mg/l. The concentrations of Chromium (Cr) in the study were 0.241±0.001 in W_A and 0.242±0.002 in U_B, while U_C was 0.233±0.004 and the control and mean were 0.373±0.095 and 0.239 mg/l respectively.

Table 4. Heavy Metal Content of Tweni (T) Study Station

	Study Stations					
Heavy metals (mg/l)	T_A	T_B	T_C	Control	Mean	Standards (WHO, mg/l)
Hg	<0.001	<0.001	<0.001	<0.001	<0.001	0.006
Cd	0.163±0.013	0.163±0.013	0.108±0.026	0.128±0.012	0.145	0.003
As	<0.001	<0.001	<0.001	<0.001	<0.001	0.010
Cu	0.193±0.018	0.193±0.018	0.114±0.037	0.128±0.028	0.167	2.000
Pb	0.013±0.002	0.014±0.001	0.021±0.004	0.016±0.000	0.016	0.010
Cr	0.263±0.021	0.263±0.021	0.352±0.042	0.373±0.057	0.293	0.050

Source: Field Work (2021)

Table 4 showed that Hg and As in all the sampled stations recorded values below 0.001 mg/l. Stations T_A, T_B and T_C for Cd recorded 0.163±0.013, 0.163±0.013, 0.108±0.026 respectively while the control station was 0.128±0.012 and the mean was 0.145 mg/l. Copper (Cu) recorded respectively 0.193±0.002 (T_A), 0.193±0.018 (T_B), 0.114±0.037 (T_C) and control as 0.128±0.028 while the mean was 0.169 mg/l. Lead (Pb) in stations T_A and T_B recorded concentrations of 0.013±0.002 and 0.014±0.001, while T_C had 0.021±0.004, control station had 0.016±0.000 while the mean was 0.016 mg/l. The concentrations of Chromium (Cr) in the study were 0.263±0.021 in T_A and same 0.263±0.021 in T_B, while T_C was 0.352±0.042 and the control and mean were 0.373±0.057 and 0.293 mg/l respectively.

Table 5. Heavy Metal Content of Shellikiri (S) Study Station

Heavy metals (mg/l)	Study Stations					Standards (WHO, mg/l)
	S_A	S_B	S_C	Control	Mean	
Hg	<0.001	<0.001	<0.001	<0.001	<0.001	0.006
Cd	0.131±0.001	0.131±0.001	0.124±0.004	0.128±0.000	0.129	0.003
As	<0.001	<0.001	<0.001	<0.001	<0.001	0.010
Cu	0.187±0.011	0.188±0.010	0.233±0.021	0.213±0.007	0.203	2.000
Pb	0.022±0.019	0.021±0.020	0.103±0.038	0.016±0.023	0.049	0.010
Cr	0.496±0.061	0.497±0.062	0.237±0.122	0.373±0.026	0.410	0.050

Source: Field Work (2021)

Table 5 showed that Hg and As in all the sampled stations recorded values below 0.001 mg/l. Stations S_A, S_B and S_C for Cd recorded 0.131±0.001, 0.131±0.001, 0.124±0.004 respectively while the control station was 0.128±0.000 and the mean was 0.129 mg/l. Copper (Cu) recorded respectively 0.187±0.011 (S_A), 0.188±0.010 (S_B), 0.233±0.021 (S_C) and control as 0.213±0.007 while the mean was 0.203 mg/l. Lead (Pb) in stations S_A and S_B recorded concentrations of 0.022±0.019 and 0.021±0.020, while S_C had 0.103±0.038, control station had 0.016±0.023 while the mean was 0.049 mg/l. The concentrations of Chromium (Cr) in the study were 0.496±0.061 in S_A and 0.497±0.021 in S_B, while S_C was 0.237±0.112 and the control and mean were 0.373±0.026 and 0.410 mg/l respectively.

Table 6. Heavy Metal Content of Esenfakiri (E) Study Station

Heavy metals (mg/l)	Study Stations					Standards (WHO, mg/l)
	E_A	E_B	E_C	Control	Mean	
Hg	<0.001	<0.001	<0.001	<0.001	<0.001	0.006
Cd	0.135±0.008	0.135±0.008	0.103±0.015	0.103±0.015	0.124	0.003
As	<0.001	<0.001	<0.001	<0.001	<0.001	0.010
Cu	0.189±0.013	0.190±0.014	0.131±0.028	0.131±0.028	0.170	2.000
Pb	0.028±0.001	0.028±0.001	0.032±0.001	0.032±0.001	0.029	0.010
Cr	0.372±0.063	0.373±0.064	0.104±0.127	0.104±0.127	0.283	0.050

Source: Field Work (2021)

Table 6 showed that Hg and As in all the sampled stations recorded values below 0.001 mg/l. Stations E_A, E_B and E_C for Cd recorded 0.135±0.008, 0.135±0.008, 0.103±0.015 respectively while the control station was 0.103±0.015 and the mean was 0.124 mg/l. Copper (Cu) recorded respectively 0.189±0.013 (E_A), 0.190±0.014 (E_B), 0.131±0.028 (E_C) and control as 0.131±0.028 with the mean as 0.170 mg/l. Lead (Pb) in stations E_A and E_B recorded concentrations of 0.028±0.001 and 0.028±0.001, while E_C had 0.032±0.001, control station had 0.032±0.001 and the mean was 0.029 mg/l. The concentrations of Chromium (Cr) in the study were 0.372±0.063 in E_A and 0.373±0.064 in E_B, while E_C was 0.104±0.127 and the control and mean were 0.104±0.127 and 0.283 mg/l respectively.

Discussion of Findings

1. Mercury (Hg)

The concentration of Hg was uniform at <0.001 mg/l which was also lower than permissible limits for contamination (EC, 1998; WHO, 2004; USEPA, 2009). Oribhabor and Ogbeibu [46] (2010) found Hg levels of approximately 0.01 mg/l in the study of concentration of heavy metals in a Niger Delta Mangrove creek, Nigeria which is a similar environment to this study. In a similar study by Nwankwoala *et al*. (2013) for heavy metal investigation in ground water sources in Yenogoa, Bayelsa, Nigeria, a range of 0.07-0.78

was recorded. This was also asserted by that of Ekpete *et al*. (2019) on the Silver River in Southern Ijaw, Bayelsa State. These values were all higher than those of this study showing that the impact of the crude oil spill was negligible on the rise of Hg level in the Santa Barbara River. This may be connected with the flow pattern of the River and most likely from the dilution effect over time as this study was done some months after the spill (Post spill variation study).

Mercury (Hg) is known to be highly toxic to humans and aquatic life, causing liver and kidney problems in addition to genotoxic carcinogenic effects (Oliveira *et al.,* 1987; Tchounwou *et al.*, 2003; Nguyen *et al*., 2005; Li *et al*., 2010; Park & Zheng, 2012). The major sources of mercury by natural sources include volcanoes, geothermal springs, geologic deposits and the ocean. Anthropogenic sources primarily include coal combustion, waste incineration, industrial uses, and mining. But in the United States, the main source of Hg to most aquatic environments is from atmospheric deposition such as rain, snow, and as dry particles.

Some water bodies also receive mercury from direct discharge of industrial wastes (cement plants), mining wastes, or naturally occurring mercury minerals, sewage, agricultural, medical products, sediments, cement plants and fly ashes *etc* (Clarkson, 1997). The major source of mercury contamination may be natural and industrial as Hg is a highly poisonous metal which is mostly found in the environment. The overdose toxic effect of mercury on thyroid gland, gastrointestinal tract, neurological and reproduction may sometime be lethal (Verma *et al*., 2018).

2. Arsenic (As)

The concentration of Arsenic (As) showed a mean value of < 0.001 mg/l all through the sampled stations which is also less than the stipulated permissible limits of 0.010mg/l (EC, 1998; WHO, 2004; USEPA, 2006; USEPA, 2009). This was also less than the range of 0.01-1.00 mg/l recorded in similar studies in Yenogoa during the investigation of heavy metals in the groundwater as control (Nwankwoala *et al*., 2013). Arsenic is a trace element found at variable concentrations in the atmosphere, soils and rocks, natural waters such as rivers (Izah & Srivastav, 2015). Some of the foods produced with arsenic have a concentration above the standard limit which could lead to health related effects especially canned foods within ranges of 0.011(Chinchin malt milk drink, Germany)-0.161 (Picnic soyamilk, Maeil). Arsenic could be leached into the environment through natural processes and anthropogenic activities such as burning of industrially generated solid wastes (Garba *et al*., 2008; Musa *et al*., 2008). Arsenic is one of the major pollutant that is deleterious to the environment and humans that consumes the contaminated water (Izah & Srivastav, 2015). Arsenic has the potential to variations due to oxidation-reduction, ligand exchanges and bio-transformations (Izah & Srivastav, 2015).

The concentration of As in surface water ranges between 0.003 and 0.477 mg/l which is higher than that found in this study (Usman & Lar, 2013). Concentration of As in the Niger Delta is relatively lower than those found in the Northern region of Nigeria due to the larger natural deposits in the soils as in areas of bedrock sulphide mineralization or mining activity, industrial contaminations, or areas affected by geothermal activity and in surface waters that are fed by high-arsenic groundwater (British Geological Survey, 2008). Lack of these activities in the study area can be responsible for the concentration in the Santa Barbara River, Nigeria. Arsenic pollution has been reported severally in the Northern part of Nigeria which has never been in the oil rich Niger Delta of Nigeria (Garba *et al*., 2008;Garba *et al*.,2010; Garba *et al*., 2012a; Garba *et al*., 2012b).

3. Cadmium (Cd)

This study recorded a range of 0.112-0.145 mg/l which was higher than those of heavy metal study in Niger Delta Creek, Buguma, Nigeria of range 0.01-0.11mg/l and the Warri river, Delta State, Nigeria as 0.00-0.05 mg/l respectively (Oribhabor & Ogbeibu, 2010; Wogu & Okaka, 2011). The concentration of Cd so recorded in the study is higher than those of WHO (2011) and NIS (2007) maximum permissible limits (0.03 and 0.003 respectively). According to Nwankwoala *et al*. (2013), groundwater around Yenogoa had smaller lower range concentration of Cd than the water of Santa Barbara River but higher upper range of 0.03-1.00 mg/l. This area did not have recent oil spill though similar terrain may be associated with the Ateo Oil Spill as no serious anthropogenic activities are prevalent. This is out rightly converse to those recorded by Ekpete *et al.* (2019) in the Silver River of Southern Ijaw, Bayelsa State, Nigeria which had range of 0.714-2.414mg/l where recent oil spills were absent. This result shows that the presence of Cd in the study water body may be from natural background than anthropogenic inputs. These

results are in consonance with the works done earlier in Ede, Opa and Asejire reservoirs, Osun State, Nigeria (Ogunfowokan *et al.,* 2010). This shows that there is gradual increase in Cd contamination and which may bio-accumulate in marine organisms which indirectly affects humans.

Cadmium is a highly toxic metal, non-essential element, chief contaminant in aquatic ecosystems due to the solubility property with adverse effects on living organisms (Benavides *et al*., 2005; Deevika *et al*., 2012). According to Uzoekwe and Achudume (2011), Cd is taken as a cumulative toxin due to the human body's ability to excrete only about 0.001% of the total ingested per day. The comparatively higher concentrations of Cd recorded in all sampling stations could be due to geologic formation of the soil and anthropogenic activities in the river area especially the recent oil spillage as no run-off from agricultural activities (Umar *et al*.,2001; Ogunfowokan *et al*., 2010). This increased level of Cd in the water relative to regulatory permissible limits is of immense challenge as the use of water high in cadmium could cause adverse health effects including renal diseases, cancer and bone pain (Itai-itai disease) and also could lead to mutagenic and teratogenic effects (Kjellstroem, 1985; Stoeplpler, 1991; Ogunfowokan *et al*., 2010). According to Akoto *et al*. (2019), Cd exposure may create deleterious health effects such as lung cancer, kidney damage, and bone fractures.

4. Lead (Pb)

The mean range of Pb (mg/l) across the study stations was 0.011 (Uwanga)-0.049 mg/l (Shellikiri). This is similar to earlier work on heavy metals in Niger Delta Mangrove Creek and Warri River where the ranges were 0.01-0.61mg/l and 0.00-0.001mg/l respectively (Oribhabor & Ogbeibu, 2010; Uzokwe & Achudume, 2011; Wogu & Okaka, 2011). This values were below, so within the permissible limits of WHO, USEPA and NIS standard (NIS, 2007; USEPA, 2009; WHO, 2011).This was lower than that observed in the Silver River of Southern Ijaw, Bayelsa State, Nigeria within the range of 1.742-3.812 mg/l (Ekpete *et al.,* 2019).This lower concentration recorded in this study compared to similar Mangrove ecosystem indicates that the recent oil spill was not the primordial factor but from natural background composition of the area. This could be proved by the higher concentration in control environments such as ground water away from the source and prone impact areas such as Yenogoa whose range was reported earlier (Ekpete *et al.,* 2019). This also meant that the oil spill may not contain serious anthropogenic inputs of Pb. According to earlier research and guidelines, Pb is classified as potentially hazardous to most forms of life, and is considered toxic and relatively accessible to aquatic organisms even at low concentrations (USEPA, 1986; Aladesanmi, 2014).

According to other research studies, most probable source of Pb in Rivers may be due to Pb particulate from the combustion of leaded gasoline, corrosion of lead-containing materials and burning of building and electronic wastes with residue washed into rivers which is obtainable in this area of study (Adesiyan *et al.,* 2018). Low lead concentrations can cause fish suffocation due to coagulated mucous formation and behavioural variations and impaired intelligent quotient in humans (Ogunfowokan *et al.*, 2010; SAWQG, 1996).

5. Chromium

The mean range of chromium (mg/l) recorded in this study was 0.222 (Worokuma)-0.410 (Shellikiri). This value range was by far higher than permissible limits of regulatory agencies [43, 44, 67, 45] (EC, 1998; WHO, 2004; NIS, 2007; USEPA, 2009). This though was higher than the lower mean range but lower than the upper mean range observed by Oribhabor and Ogbeibu (2010) in their study of heavy metals in a typical Niger Delta Mangrove Creek in Nigeria precisely Buguma in Rivers State, Nigeria. The concentration of Cr in this study was also found to be higher than those of rivers studied by Adesiyan *et al.* (2018) in South-western Nigeria where oil exploration is absent meaning some oil spill inputs can be anthropogenic and those of Uzoekwe and Achudume (2011) in similar research. This slight increase may be attributed to natural seepages and remains of floating oil sheens found which may be components of exploratory chemical mixtures from crude oil.

Chromium is one of the heavy metals known to be highly toxic to humans and aquatic life leading to liver and kidney complications and genotoxic carcinogens (Nguyen *et al.*, 2005). The sources of Cr in this study are mostly unlikely to emanate from waste consisting of lead-chromium batteries, coloured polythene bags, discarded plastic materials and empty paint containers as these are not readily available here except empty plastics as earlier posited (Jung *et al.*, 2006). The pristine source of Cr is the Cr (III) which provides micronutrients for humans and play a vital role in the metabolism of lipids and

sugars Oliveira (2012), but the Cr (VI) a product of oxidation can be released into rivers which are declared carcinogenic for human health (Tchounwou, 2012).

6. Copper (Cu)

The observed range of copper (mg/l) in this study was 0.159 (Uwanga)-0.204 (Worokuma). This is far below the permissible limits of 1.3 (USEPA, 2009), 2.0 (WHO, 2004), 1.5 (BIS) and 1.00 (NIS, 2007) as standard regulations. The concentration of Cu in this sampled Santa Barbara River was extremely lower than those observed for the Warri and Silver Rivers within similar environment, 2.171-3.691 mg/l (Wogu & Okaka, 2011; Ekpete *et al.*, 2019). This was also higher than those observed by Uzoekwe and Achudume (2011) in similar terrain. This was within similar range of control from ground water in Yenogoa, Bayelsa State, Niger Delta, Nigeria. The low level of Cu in the study locations is an indication of reduced anthropogenic inputs from industrial and commercial activities. Oil spills in the Niger delta have acute and long-term effects on human health (Ordinioha, & Brisibe, 2013). The major sources of Cu in water bodies are natural sources of copper in aquatic systems including geological deposits, volcanic activity, and weathering and erosion of rocks and soils. During the rainy season, non-point sources such as urban run-off are believed to be the major source of copper in both cases (Sodre *et al.*, 2005). Copper toxicity can occur from eating acid food cooked in uncoated copper cookware or from exposure to excess copper in drinking water or other environmental sources (Nwineewii & Edem, 2014). Chronic copper exposure can damage the liver and kidneys (ARD-EHP-9, 2005).

According to the World Bank (1990) findings, the maximum level of copper in liquid effluents from the Petrochemicals Company was 0.5mg/l while specifically the EIA by Eleme Petrochemicals Company in 1992 showed that water analysis for Cu was found to be 0.1mg/l. These values show the input from crude oil related industrial activities which was supposed to be similar to those of the study but were found to be higher meaning some anthropogenic inputs abound. Figure 2 is the illustration of the trends of heavy metal concentrations across the five study stations of W, U, T, S and E. Similarly, the comparison of the mean concentration of heavy metals and the WHO standard permissible limits is shown in Figure 3.

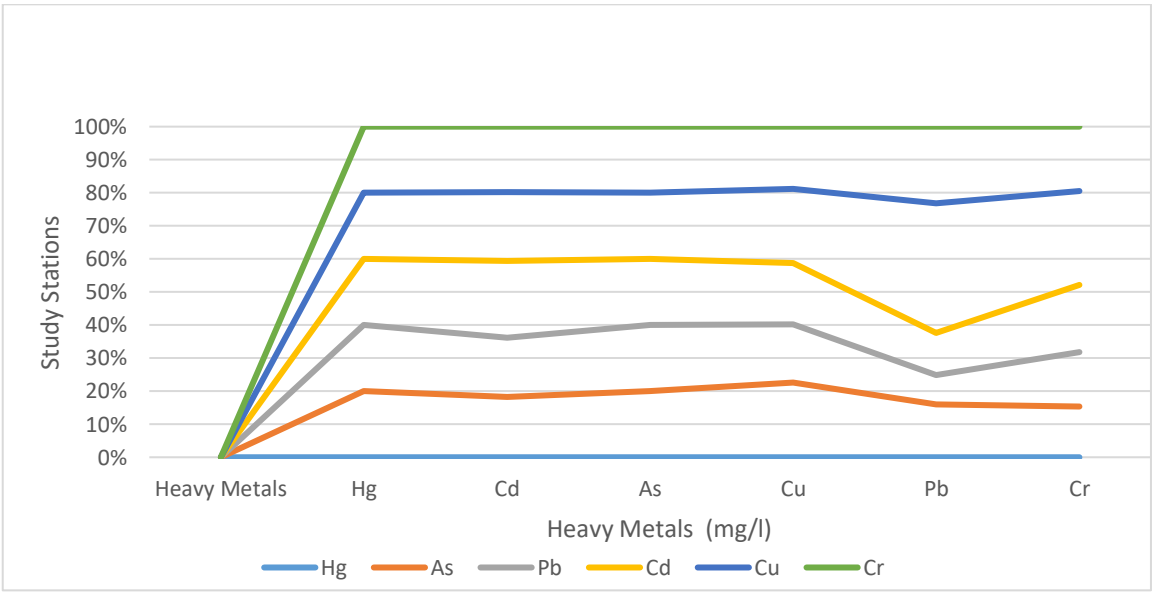

Figure 2. Trend of Heavy Metal Concentration across the Study Stations

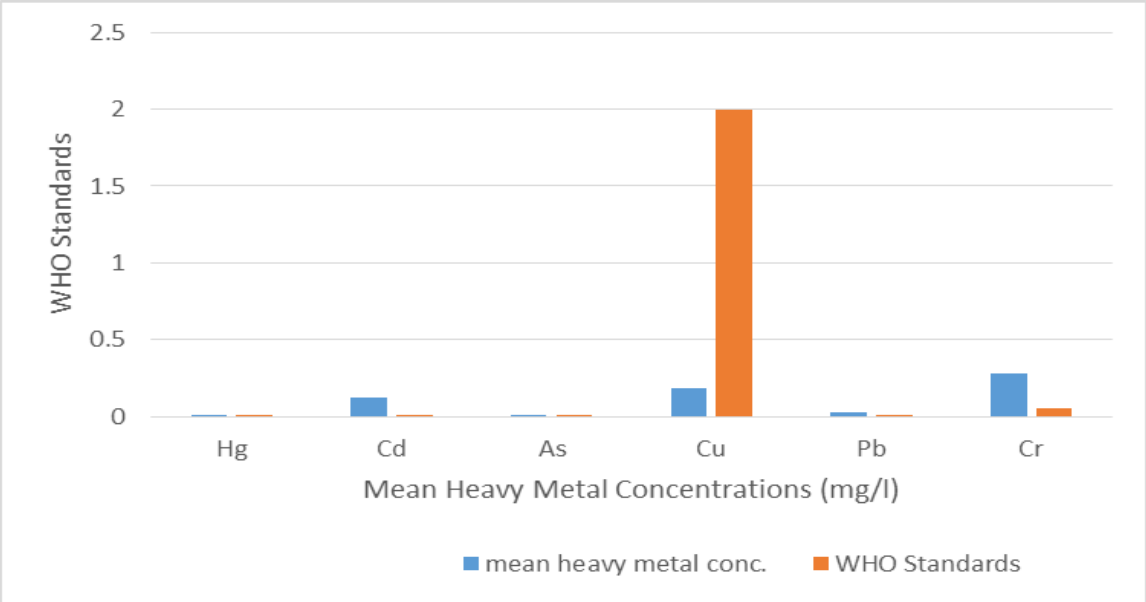

Figure 3. Comparative Mean Concentration of Heavy Metals and WHO Standards

Table 7. Contamination Factor across the Study Stations

	Study Stations				
Heavy Metals (mg/l)	W	U	T	S	E
Hg	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Cd	0.891	0.875	0.883	1.008	1.204
As	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Cu	0.958	0.746	1.305	0.953	1.300
Pb	1.250	0.688	1.000	3.063	0.906
Cr	0.595	0.641	0.786	1.100	2.721

Source: Field work (2021)

Table 8. CDI, HQ, ILCR, ErF, RI and HI for Heavy Metals in Adults (Ad) and Children (Ch)

Heavy metals/HQ	Stations									
	W		U		T		S		E	
	Ad	Ch	Ad	Ch	Ad	Ch	Ad	Ch	Ad	Ch
Cd (CDI)	0.0031	0.073	0.003	0.072	0.004	0.093	0.004	0.083	0.003	0.079
HQ_{Cd}	6.20	146	6.00	144	8.00	186	8.00	170	6.00	158
ILCR	0.019	0.445	0.018	0.439	0.024	0.567	0.024	0.506	0.019	0.482
ErF	27		26		26		30		36	
RI_{Cd}	149									
Cu (CDI)	0.006	0.135	0.004	0.102	0.005	0.107	0.006	0.130	0.005	0.108
HQ_{Cu}	0.15	3.38	0.10	2.55	0.13	2.68	0.15	3.25	0.13	2.70
ILCR	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
ErF	5		4		7		5		7	
RI_{Cu}	26									
Pb (CDI)	0.001	0.013	0.000	0.007	0.000	0.010	0.001	0.031	0.001	0.019
HQ_{Pb}	0.29	3.70	0.00	2.00	0.00	2.86	0.29	8.86	0.29	5.43
ILCR	0.009	0.111	0.000	0.060	0.000	0.085	0.085	0.264	0.009	0.162
ErF	6		3		5		15		5	
RI_{Pb}	35									

Cr (CDI)	0.006	0.142	0.007	0.153	0.008	0.187	0.011	0.262	0.008	0.181
HQ_{Cr}	20.00	473	23	510	27	623	37	873	27	603
ILCR	0.246	5.822	0.287	6.273	0.328	7.667	0.451	10.740	0.328	7.421
ErF	1		1		2		2		5	
RI_{Cr}	12									
HI	6.50	626	31	659	35	815	45	1055	33	769

Source: Field Work (2022)

[Where CDI-Chronic Daily Intake; HQ-Hazard Index; ILCR-Incremental Lifetime Cancer Risk]

Risk Assessment

The Hazard Quotient (HQ) calculated for Cd in the Santa Barbara River had values greater than 1 (HQ > 1) for adults in E (6.0) and children in T (186). Cu also had HQ of > 1 in W for children while Pb had a maximum HQ > 1 (8.86) for children in E. The highest HQ values were observed for Cr both for adults (Worokuma, 20) and children in station E (873). The results for the HQ showed that of all the cases considered, Cu had the highest HQ for children, however, were above the threshold value of risk as HQ < 0.01 indicates no existing risk (Clarke *et al.*, 2016). These values being greater than one shows serious concern as likely adverse health effects are imminent. This also meant obvious risk but adverse non-carcinogenic effect. These values for HQ were by far higher than those obtained by Zakir *et al.* (2020) for Cu, Pb, Cr and Cd in water and irrigation water in the Jamalpur Sadar area in Bangladesh. Similarly, the HI for both adults and children were higher than those obtained in similar risk assessment studies (Karimi *et al.*, 2020; Zakir *et al.*, 2020).

The hazard index (HI) indicate that in all the stations calculated values of greater than one (HI >1) which meant that the probability of non-carcinogenic effects occurring and increases as HI increases occurs. This means carcinogenic risk via direct ingestion of water. HI values were extremely higher in children relatively as is found in stations W (626), U (659), T (815), S (1055) and E (769). No station recorded HI < 1 except in W for adults having 6.50 as the least. This is of great concern. The carcinogenic risk via ingestion for all the stations were above the remedial goal target of 1.0×10^{-6}. Total hazard index values from heavy metals through three exposure routes for adults and children in farmlands were 9.13E−01 and 1.10 respectively, indicating that there was non-carcinogenic risk for children which was far lower than the study result of the Santa Barbara River (Karimi *et al.*, 2020).

Health risk assessment for all the sites indicated dangerous single heavy metal and their cumulative effect indicated by the HI calls for major concern as all highly exceeded the threshold value of 1. This was observed to be relatively higher in children exposed to the river water by ingestion as the source of contamination was more geogenic than anthropogenic [91] (Onyele & Anyanwu, 2018). The hazard quotients (HQ) and the hazard index (HI) value levels of studied heavy metals (Cu, Cr, Cd, As) in all sampling sites did not exceed the acceptable risk limits of non-carcinogenic value [92] (Liu *et al.*, 2018).

The pollution levels were determined using PLI, EF, CDI and CF. The Pollution Load Index (PLI) for Cd was calculated and it recorded the highest risk index of (PLI) of 149 (> 5). All the detectable metals had risk index of greater than 5 but the highest was found in the order, Cd> Pb > Cu > Cr (149, 35, 26 and 12 respectively) which meant extremely high level of pollution. This was comparable to pollution levels (PLI) of heavy metals in soil which showed heavy metal contamination of agricultural soils (Iyama *et al.*, 2021; Karimi *et al.*, 2020). This was lower for similar studies of PLI in heavy metals having ranges of 0.00-1.14 and 0.45-1.15 showing no pollutions respectively (Saha & Hossain, 2011; Salah *et al.*, 2012; Rahman *et al.*, 2022) .These values were far lower than those recorded in this study which was considered polluted from PLI results.

In order to determine the likely natural or anthropogenic input and impact in the Santa Barbara River, enrichment factor (EF) was calculated. The Enrichment Factor (ErF or EF) for station U had minimum value of 26 and maximum ErF for Cd in station E as 36 which showed that it was very high (20-40) [96] (Jimoh, 2017). Copper (Cu) had a maximum E_rF of 7 in E which showed significant E_rF as earlier corroborated [96] (Jimoh, 2017). This was similar to minimum value of 3 in station U for Pb and maximum of 15 in station S indicating significant enrichment. This was moderate (2-5) as was found in the minimum values of E_rF found for Cr in station W as 1 and maximum of 5 in station

E.This showed moderate enrichment factor (Jimoh, 2017). This was found to be higher than EF recorded for heavy metals (Cd, Pb and Cu) studied in similar research works (Daka *et al*., 2007; Elias *et al*., 2014; Mamat *et al*., 2016).

The Incremental Lifetime Cancer Risk (ILCR) for Cadmium (Cd), Pb and Cr recorded calculated values above the maximum limits of 1.0×10^{-4} in all the stations especially for adults in station U (0.018) and children in station S(0.567) for cadmium. Similarly, Pb for adults in station U and T recorded 0.000 but 0.264 for children in station E indicating carcinogenic health risk for single element (USEPA, 2010; Hadzi *et al*., 2015; Mohammadi *et al*., 2019). Chromium (Cr) had a minimum value of 0.246 in adults for station W and 10.74 in station E for children (10.74) which was of a very high carcinogenic risk. The calculated values from the concentrations of these heavy metals remains a source of threat to public health if ingested from drinking water for Cd, Pb and Cr. The ILCR is the probability that one can have cancer over a 70-year lifetime due to 24-hour exposure to any potential carcinogen as heavy metals (Adamu *et al*., 2015). The results were relatively higher than those of Zakir *et al*. (2020) which were Pb (5.03 E-09), Cr (9.16 E-08) and Cd (4.51E-06).

The chronic daily intake (CDI) for Cd ranged between 0.003 and 0.093 which showed values higher than the oral reference dose of 0.001 mg Cd Kg/day. This is not friendly as it surpasses the oral daily intake as Cd is known to be very dangerous and of non-carcinogenic risk factor. Similarly, copper (Cu) had upper limit above the oral reference dose of 0.135 and lower limit of 0.04 which was also the oral reference dose for Cu (USEPA IRIS, 2011). This is on the threshold which meant that there is a high risk factor. These values were relatively higher than those recorded by Zakir *et al.*(2020) for health risk assessment of heavy metals and water quality in the Jamalpur Sadar area water body. The relationship that existed in CDI, HQ and ILCR is showed in Fig.4.

The contamination factor (CF) for Hg and As were below 0.001 meaning that (CF<1) there was low contamination for these metals. For Cadmium (Cd), Station W, U, T had low contamination but stations S and E (1.008 and 1.204) respectively were of moderate contamination (1< CF < 3). Copper (Cu) recorded low contamination in stations W, U and S but moderate contaminations in T (1.305) and E (1.300). Lead (Pb) recorded low contamination in stations U (0.688) and E (0.906) but station W (1.250) and T (1.000) had moderate contamination while only station S (3.063) had considerable contamination. Similarly, Chromium (Cr) had low contaminations in stations W (0.595), U (0.641), T (0.786) but S (1.100) and E (2.721) had moderate contaminations. Lead (Pb) was of moderate CDI as both lower and upper range values were within acceptable oral reference doses of 0.04 (USEPA IRIS, 2011). Chromium (Cr) poses a very high risk as the lower and upper ranges of CF were higher than the permissible reference oral doses of 0.003 Kg/ day. Chromium (Cr) had a calculated range of 0.006 – 0.262 which indicates high risk factor. The CF values obtained indicated low to moderate level of contamination similar to the works of Rahman *et al*. (2022) for river sediments. This pollution levels of heavy metals in soil samples using the contamination factor (CF) showed heavy metal contamination of agricultural soils similar to this study (Karimi *et al*., 2020). Contamination factor (CF) of Pb, Cr, Cu responsible for considerable contaminations of sediments showing low to moderate level of contamination ranged from 0.00 to 3.1 where Cr had the least was also reported earlier (Rahman *et al*.,2022).

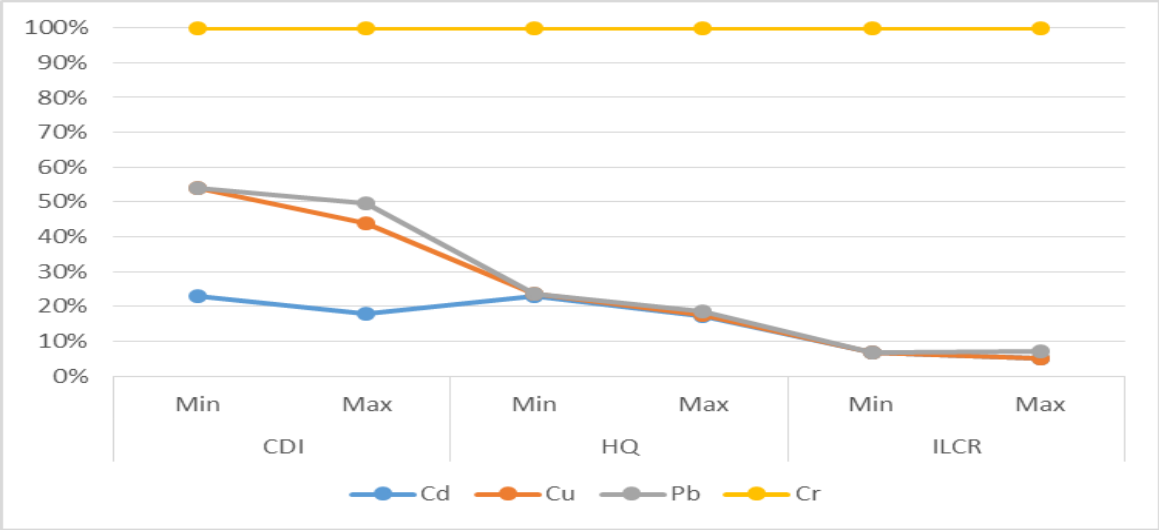

Figure 4. Relationship of CDI, HQ and ILCR for the Heavy Metals

The findings of this research showed that the rising concentration of heavy metals in the Santa Barbara River increases the toxicity in the aquatic environment hence affecting the ecosystem (Perumal *et al.*, 2021). The trend of heavy metal abundance was found in this order Cr>Cu>Cd>Pb>Hg=As. Which was almost reversed by Owamah (2013) for study of petroleum impacted River in the Niger Delta, Pb>Cu>Cd>Hg. The pollution indices showed that the heavy metal contamination was mostly due to Cd, Cu and Cr while a low and moderate level of contamination was caused by Pb, Hg, As which was a bit different from earlier similar work (Perumal *et al.*,2021). There was no statistically significant difference between groups as demonstrated by one-way ANOVA (F (4, 25) = 0.1244, p= .9723). A Tukey Post Hoc test showed that the heavy metals in stations, W, U, T, S, E were not of statistically significant concentration differences from each other respectively (p= 0.9999, .9998, .9801, .9999, .9992, .9649, .9996, .9936, .0000, .9912). Similarly, the six heavy metals measured (M= 0.1, SD = 0.06) compared to the corresponding heavy metals in the standard control (M = 0.35, SD = 3.28) showed no significantly better peak flow concentrations t (5) = -0.732, p = .240.

CONCLUSION

This study showed that the concentrations of Cd, Cu and Cr were higher than permissible limits of various standards while Hg, As and Pb were found to be at tolerable but increasing values. This is a great threat to public health as most of the indigent inhabitants depend on this for drinking due to the exorbitant cost of assumed pure or bottled water. The impact and effect of the presence of these toxic metals are not majorly from the recent oil spills probably due to the delay in time frame after the spill occurred for this study but rather due to natural soil, plant and water compositions. Chromium (Cr) poses a very high risk, as the lower and upper ranges of CF were higher than the permissible reference oral doses of 0.003 Kg/ day. The chronic daily intake (CDI) for Cd ranged between 0.003 and 0.093 which showed values higher than the oral reference dose of 0.001 mg Cd Kg/day. This is not friendly as it surpasses the oral daily intake and Cd is known to be very dangerous and non-carcinogenic risk factor. There is therefore the need for regular monitoring as to regulate the input from anthropogenic sources as oil spills may contain some of these metals in their industrial processes.

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