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Human Health Risk Assessment of Trace Metals in Water from Cross River Estuary, Niger Delta, Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. Author EBA designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author UDS managed the analyses of the study. Author AAE managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

The aim of this study was to determine the levels of some trace metals in water from Cross River estuary (CRE) and estimate the human health risk associated with water from the estuary via ingestion pathway and dermal contact. The trace metals in water were determined using atomic absorption spectrophotometer and the human health risk assessment of the trace metals was carried out using models stipulated by United States environmental Protection Agency (USEPA). The range for the results in mg/l was as follows: Pb (0.193- 0.632), Cd (0.118 - 1.084), Ni (0.048 - 0.632), Fe (0.056 - 0.921), Zn (0.063 - 0.242), Cu(0.072 - 0.146). All the investigated metals were above the WHO limit except zinc and copper. The target hazard quotient (THQ) via ingestion pathway for Pb, Cd and Ni were higher than unity. Also, the hazard indices for all the investigated metals in all the study sites were higher than unity. The target hazard quotient and Hazard index via dermal pathway were less than one for all the metal investigated, except Cd at Ebughu. Regular monitoring and minimization of anthropogenic activities resulting in elevated metal concentration is recommended.

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1. INTRODUCTION

Rapid urbanization, population growth and industrial development have generated issues relating to environmental safety and public health. Ogbonmida et al. [1] reported that man-made activities have led to continuous release of chemical pollutants including trace metals into different environmental matrices. When the quality of water changes in a way that affects organisms living in the water or suitability of water for domestic uses such as swimming, irrigation, recreation and drinking, the water is said to be polluted. Water pollution by inorganic pollutants such as trace metals affects the integrity of the ecosystem and is a threat to human health because of its bioaccumulative, biomagnification potentials and persistence in the environment [2,3].

Metals are substances with high electrical conductivity that easily lose electrons to become cations. They are known as trace metals because they are found in small amount in the environment. Transition metals such as iron (Fe), nickel (Ni), copper (Cu), and zinc (Zn) are required to maintain various biochemical and physiological functions in living organisms. Thesetrace metals are known as essential trace but at concentrations above the threshold values, they can be toxic [4]. Metals such as lead (Pb) and Cadmium are toxic at very low concentrations and are known as non-essential trace metals [5].

The sources of trace metals in the environment may be anthropogenic or natural. Anthropogenic sources of water, sediment and aquatic ecosystem contamination are industrial activities, mining and disposal of untreated and partially treated effluents containing toxic metals [6]. Monitoring of surface waters is important in order to be assured of the sustainability of ecosystem and functions of the aquatic environment [7]. In the Niger Delta, trace metals contamination by metals such as Pb, Ni, Cd, Zn, Cu, Fe and their elevated levels in the environment is primarily due to uncontrolled pollution levels linked to oil pollution, indiscriminate discharge of domestic and municipal waste, agricultural run-offs, pipeline vandalisation and oil spillage. According to Valarindis and Viachogianmi [8] Pb, Cu, Ni, and Zn are important metal toxicants from anthropogenic sources. Inengite et al. [9] reported that Pb, Ni, Cr, V areminor components of crude oil and are indices of biodegraded oil. The six metals considered in this study were selected because they are major contributors to water pollution from oil production and exploitation activities and from indiscriminate discharge of domestic and municipal waste into the river. The determination of the above-mentioned metals in the study location was also considered as result of their association in piping system, usefulness as pigment in marine corrosion inhibition for example corrosion resistant zinc plating of iron and as antiknock agents in marine automobile engines. Copper is used as component of wood preservatives in boat making process while nickel is used as an alloy in steel and in the production of nickel-cadmium battery [10]. Nickel can also be released into the environment during the combustion of fossil fuel. These metals can find their way to the food chain by direct ingestion of water or by accumulation in sea food consumed by the coastal communities leading to adverse human health effect.

The toxicity of trace metal is a function of its concentration, exposure and chemical nature. Exposure to pollutants such as trace metals through ingestion, inhalation or dermal contact can pose risk to human health [11].

Human health risk process is used to estimate the nature and probability of adverse health effects in humans exposed to contaminants in environmental media, in the immediate or the nearest future [12]. Risk assessment evaluates the consequences of human activities and weighs the adverse effect to public health against the contribution to economic development. Cross River estuary is located in the Niger Delta and all the investigated sites undertake fishing activities. The water from the estuary is used for drinking, recreational activities like swimming and irrigation in some settlements. Domestic wastes from homes, a five-star hotel and industrial waste water from a petrochemical facility located in the area are discharged directly into the river.

Several authors have reported on the levels of trace metals in some estuary in the Niger Delta [13-16]. Some researcher have worked on the risk assessment of trace metals in water from Qua Iboe river estuary [11,17,18] and Imo river estuary [19], but there is little or no information on the risk assessment of trace metals in water from Cross River Estuary. This study was conducted to assess the levels of some trace metals in water from Cross River estuary and estimate the human health risk associated with exposure to trace metal pollutants in water from the above estuary via ingestion and dermal pathway.

2. MATERIALS AND METHODS

2.1 Description of Study Area

The Cross River estuary takes it rise from Cameroon Mountain. It meanders into Nigeria and then Southwards through high rainforest formations before discharging into the Atlantic Ocean at the Gulf of Guinea. Within the lower brackish water reaches of the River, the Vegetation changes to mangrove forest. It is known as the biggest estuary in the Gulf of Guinea.

The Cross River Estuary lies between latitude of 04°10’ and 05°10’N and longitude 008°15’ and 008°35E. The five sampling sites selected for the study were: Ebughu, Ishiet, Oron and Ifiayong (Control). The four examined sites (Ebughu, Ifiayong, Ishiet and Oron) of the Cross River Estuary are linked by water ways However, in recent decades drilling fluids and large amount of industrial waste water from oil exploitation activities close to the examined sites, domestic wastes and sewage have been released into the Cross River Estuary. The control site relatively free from oil exploration activities is about 30km from the other sites. Figure one shows a map of the study area indicating the sampling sites (study locations).

2.2 Sample and Sampling

Surface water samples were collected from the selected locations with 500 ml sterilized polyethylene bottle according to the method of APHA [20]. Sampling was conducted monthly from May, 2019 to July, 2019. The samples from five sampling points per sampling sites were homogenized to form a composite sample. High purity nitric acid was added immediately after collection of water samples to stabilize the samples. Samples were refrigerated at 4°C prior to analysis.

2.3 Determination of Trace Metals

The water samples and reagent blank were digested using nitric acid (HNO_3) for the determination of metals ions concentration before analysis with atomic absorption spectrophotometer as described by Akan et al. [21]. This was necessary to destroy the organic matrix which can trap the trace metals and making unavailable for the instrumental analysis. After appropriate digestion, the trace metals were determined using Buck atomic absorption spectrophotometer (Unicam 939/959 model). All the analyses were performed 2 days after each sampling. Before the determination of any sample, a calibration curve was prepared from a standard stock solution of the metal; buck certified standards were used for the respective trace metals while the working solution was prepared by dilution of the stock solution. A hollow cathode lamp for each of the metal was used for each analysis. Each of the working standards was sprayed or aspirated into the flame and the corresponding absorbance for each concentration was recorded. A blank was similarly determined. Blanks were used to reset the instrument prior to each analysis to avoid matrix interference. The analysis was carried out three times for reproducibility, accuracy and precision

2.4 Statistical Analysis

All values were expressed as mean of three determinations ± standard deviation. One way ANOVA was performed using Excel spreadsheet of window 10 to compare the means between stations and a $P < 0.05$ was considered statistically significant. Pearson’s correlation analysis and Hierarchical cluster analysis were performed using SPSS statistics version 22 for windows.

2.5 Health Risk Assessment

Human health risk assessment is a process that involves the characterization of the probability of adverse human health effect associated with exposure to environmental chemicals according to Integrated Risk information system (IRIS) [22]. Different models have been postulated by USEPA [23] for different pollution pathway. The model in equation (1) was postulated by USEPA [23], while the model in equation (2) was proposed by [22,24].

2.5.1 Pollution pathway

Usually pollutants gain entry into the body through different exposure or contact pathways which include inhalation, ingestion and dermal contacts.

2.5.2 Ingestion pathway

A typical risk for oral exposure (ingestion) of some trace metals may be defined by the equation below:

$$\text{CDIingestion} = \frac{\text{C x IR x EF x ED}}{\text{Bw x AT}} \qquad (1)$$

Where,

$\text{CDI}_{\text{ingestion}}$= Chronic daily intake via ingestion (mg/kg/ day)
C = Concentration of trace metal or other pollutants in water (mg/l),
IR = Drinking water ingestion rate (l/day)
EF = Exposure frequency (days/year)
ED = Exposure duration (year)
Bw = Body weight (kg)
AT = Average time

2.5.3 Dermal contact pathway

$$\textbf{CDI}\ \text{derm} = \frac{\text{Cw x SA x Kp x ET x EF x ED}}{\text{Bw x AT}} \qquad (2)$$

Where,

CD1derm = Chronic daily exposure dose through dermal contact of water (mg/kg/ day)
Cw = concentration of pollutants in drinking water (mg/l)
SA = Drinking water exposed skin area (cm^3)
Kp = Dermal permeability coefficient (cm/hr)
ET = exposure time during bathing and shower (min/day)
EF = Exposure frequency (days/year)
ED = Exposure duration (year)
Bw = Body weight (kg)
AT = Averaging time (days)

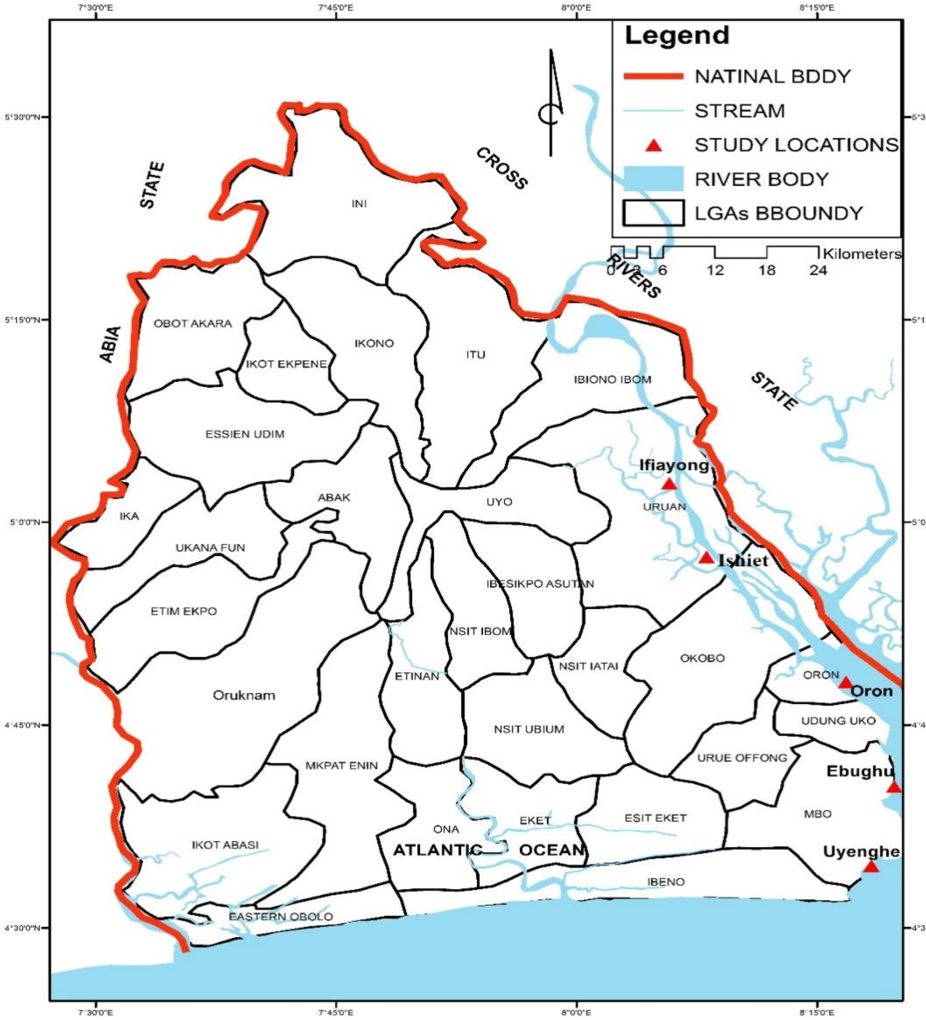

Fig. 1. Map of Akwa Ibom state showing the study area
(Source: ministry of Lands and Housing. Department of Cartography)

Table 1. GPS coordinates of sampling locations along from Cross River Estuary

Study location	Longitude (E)	Latitude (N)
Ebughu	8.32470	4.6786
Ishiet	8.1357	4.9555
Oron	8.2770	4.7887
Uyenghe	8.30533	4.5726
Ifiayong	8.096904	5.04701

2.6 Non-Carcinogenic Risk Assessment

Non-carcinogenic risk of some trace metal in water may be predicted from their target hazard quotient (THQ) and hazard index (HI) indices as shown below:

$$\mathrm{THQ\ ing} = \mathrm{CDing} / \mathrm{RfD} \quad (3)$$

$$\mathrm{THQ\ derm} = \mathrm{CDderm} / \mathrm{RfD} \quad (4)$$

CDI ing = chronic daily intake via ingestion (mg/kg /day)
CD derm = chronic daily exposure dose through dermal contact of water (mg / kg /day)
RfD = reference dose of the contaminant (mg /kg/ day)

The values for Hazard index (HI) was obtained from the model below according to the following authors: USEPA [25], Naveedullah et al. [26], and Maigairi et al. [27].

$$\mathrm{HI} = \mathrm{THQ}_{(\mathrm{Toxicant\ 1})} + \mathrm{THQ}_{(\mathrm{Toxicant\ 2})} + \ldots\ldots\ldots\ldots \mathrm{THQ}_{(\mathrm{Toxicant\ n})} \quad (5)$$

If the THQ and HI exceed 1 there might be concerns for non-carcinogenic risk, which indicates potential adverse effect on human health. HI is the sum of THQs from all applicable pathways and different pollutants. It is used to evaluate the total potential non-carcinogenic risk posed by more than one pathway and more than one pollutant.

3. RESULTS

The mean concentrations of trace metals in water from Cross River Estuary (CRE) sampled from five locations are presented in Table 2. The mean concentration of the trace metals ranged from 0.048 mg/l at Ifiayong to 1.53 mg/l for nickel at Oron. The trend for the variation of the metals was Ni > Cd > Pb > Fe > Zn > Cu. One way analysis of variance (ANOVA) at 95% confidence level, using Microsoft excel showed significant differences between the five sampling sites. ($P < 0.05$).

The target hazard quotients of some trace metals in water via ingestion pathway from CRE ranged from 4.885 at the control site to 30.975 for Ebughu as summarized in Table 3. The highest value was recorded for Cd at Ebughu while the lowest value was recorded for zinc at the control. The trend for the variation of THQ via ingestion pathway was Cd > Pb > Ni > Cu > Fe > Zn. The target hazard quotients of some trace metals in water via dermal contact from CRE ranged from 0.287 at the control site to 1.326 for Ebughu as summarized in Table 4. The trend for the variation of THQ via dermal contact pathway was Cd > Cu> Ni > Pb > Fe >Zn. The highest value was recorded for Cd at Egbuhu and the least value was recorded for iron at the control site.

Strong positive correlation was observed between Cd-Pb ($r = 0.910$), Fe-Pb ($r = 0.916$), Zn-Fe ($r = 0.925$), Cu-Ni ($r = 0.902$) as shown in Table 5. The possible similarities between the investigated trace metals and sampling sites based on source apportionment are presented in Fig. 2 and Fig. 3.

4. DISCUSSION

The concentrations of Pb, Cd, Ni were higher than values reported by Moses and Etuk [11] while the concentrations of Fe, Zn and Cu were lower than values reported by the above authors for trace metals in water from Qua Iboe river estuary. Benson et al. [17] reported values comparable to the result in this study. The concentrations o0f Fe, Pb, Cd and Ni exceeded the permissible limit stipulated by the world health organization [28].

The high level of lead might be due to anthropogenic activities such as marine transportation, direct discharge of wastes from oil facilities within the study area and introduction of lead laden domestic waste into the water body. Moses and Etuk [11] reported that lead in marine environment is associated with oil exploration, pipeline transportation as well corrosion inhibition. Renal failure has been linked with the ingestion of drinking water polluted with lead. Howard et al. [29], stated that high concentration of lead in the body can result in permanent damage to the central nervous system and kidney. Sankla et al. [30], linked stunted growth, nervous system damage, learning disabilities, crime and antisocial behavior in children to lead toxicity. Edokpayi et al. [31], described possible correlation between lead exposure and mental and physical retardation in children under six.

The concentration of Cd in this study was between 2 to 20 times higher than the WHO stipulated standard. Benson et al. [17], reported values higher than this study for Douglas creek. High level of cadmium has been implicated in kidney defect and loss in calcium from the bones resulting in osteoporosis and osteomalacia. According to Woodworth and Pascoe [32], Cd interferes with calcium regulation in biological systems. Elevated levels of Cd in the marine environment may be due to discharge of domestic waste containing Cadmium-nickel battery. Cadmium is also used as pigment in corrosion paint used in marine environment as it can provide good corrosion in high stress environment such as marine and aerospace.

Table 2. Mean concentrations of trace metals in water from Cross River Estuary (CRE)

Location	Pb	Cd	Ni	Fe	Zn	Cu
Ebughu	0.632±0.020	1.084±0.056	1.783±0.096	0.847±0.032	0.201±0.001	0.114±0.042
Ishiet	0.540±0.019	0.739±0.011	2.010±0.046	0.647±0.007	0.148±0.004	0.146±0.011
Oron	0.542±0.005	0.608±0.019	1.583±0.120	0.901±0.033	0.242±0.003	0.133±0.059
Uyenghe	0.511±0.034	0.483±0.178	0.715±0.004	0.921±0.002	0.177±0.002	0.110±0.006
Ifiayong	0.193±0.017	0.1186±0.009	0.048±0.002	0.056±0.001	0.063±0.004	0.072±0.003
WHO	0.05	0.05	0.02	0.3	3.0	2.0
NESREA	0.05	0.01	0.01	0.3	5.0	2.0

Table 3. Target Hazard quotient and Hazard index of trace metals in water from CRE via ingestion pathway

Location	Pb	Cd	Ni	Fe	Zn	Cu	Hazard index
Ebughu	4.500	30.894	2.540	0.034	0.019	0.810	38.795
Ishiet	3.847	21.060	2.865	0.026	0.014	0.104	27.907
Oron	3.862	17.330	2.255	0.036	0.023	0.094	23.602
Uyenghe	3.642	13.780	1.015	0.037	0.016	0.078	18.570
Ifiayong	1.375	3.380	0.068	0.002	0.006	0.051	4.883

Table 4. Target Hazard quotient and Hazard index of trace metals in water from CRE via dermal pathway

Location	Pb	Cd	Ni	Fe	Zn	Cu	Hazard index
Ebughu	0.0496	1.0406	0.0106	0.00014	4.84E-05	0.2707	1.326
Ishiet	0.0040	0.7094	0.0120	0.00011	3.55E-05	0.3474	1.072
Oron	0.0040	0.5839	0.0094	0.00015	5.82E-05	0.3161	0.9136
Uyenghe	0.0037	0.4626	0.0042	0.00015	4.26E-05	0.2612	0.7378
Ifiayong	0.0014	0.1138	0.0003	9.560E-06	1.52E-05	0.1719	0.2875

Table 5. Pearson's correlation matrix for trace metals in water from CRE

	Pb	Cd	Ni	Fe	Zn	Cu
Pb	1					
Cd	0.919*	1				
Ni	0.859	0.868	1			
Fe	0.916*	0.685	0.637	1		
Zn	0.856	0.667	0.669	0.925*	1	
Cu	0.788	0.634	0.902	0.695*	0.675	1

**Correlation is significant at 0.05 level (2-tailed)*

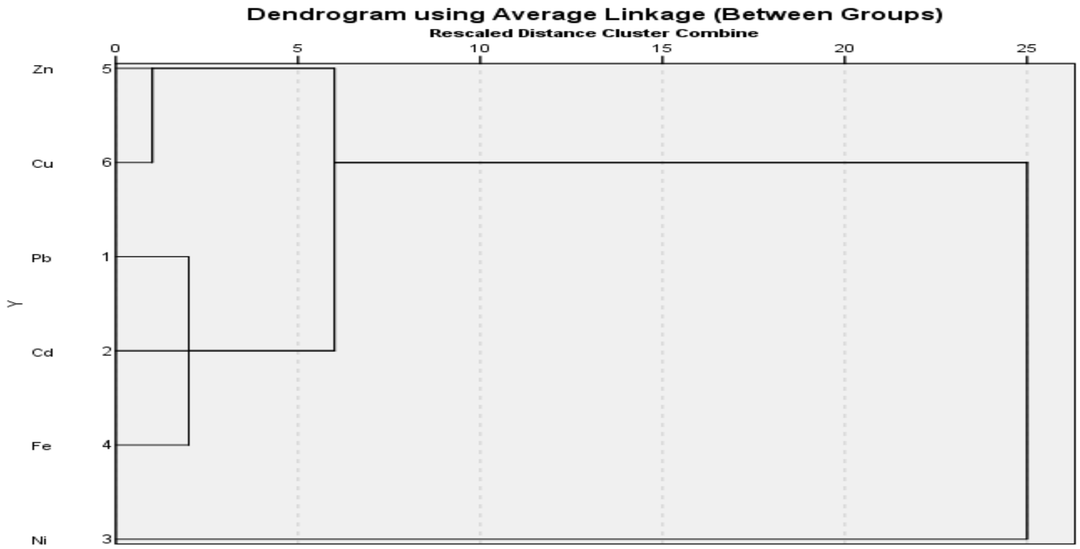

Fig. 2. Dendrogram of trace metals trends in water from the sampling sites along CRE

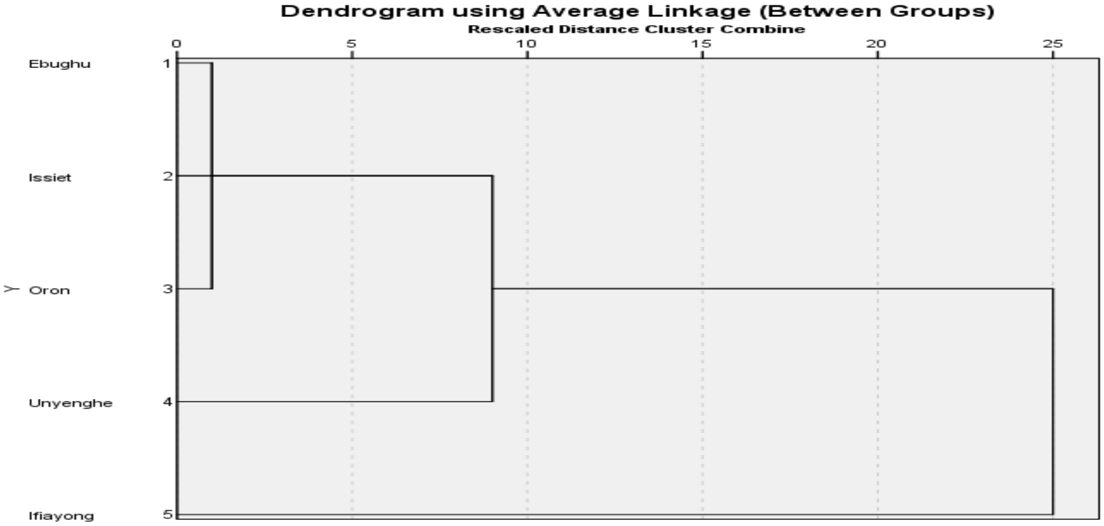

Fig. 3. Dendrogram showing possible similarities between sampling sites

Nickel in this study was higher than values reported by the following by Ebong et al. [14], Moses and Etuk [11], Benson et al. [17]. The elevated levels of nickel observed in this study might be due to the use of nickelin nickel plating for anticorrosion and in the production of batteries. Nickel is one of the trace components of crude oil and Ni-V ratio is used for the characterization of crude oil [33]. Oil exploitation or vandalisation of pipeline resulting in oil spillage can introduce nickel into the environment. High dose of nickel in rat and dog was responsible for reduction in body weight [16]. Dermal irritation, hair loss, worsening case of eczema has been linked to nickel toxicity.

High level of iron was recorded in the examined site compared to the control site. Iron is the second most abundant element in the earth crust and corroded oil pipeline and iron laden domestic waste may contribute to the observed levels in this study. Iron and nickel occur as trace metallic components in metaloporphyrin, transition metals and organometallic compounds. Iron-rich water used for washing and drinking results in unpleasant metallic taste and staining of clothes.

High levels of Fe has been linked to genetic disorder known as hemochromatosis [11,31]. In aquatic ecosystem, high iron concentrations affects the behavior, reproduction and survival of aquatic animal. It also, interferes with their metabolism and osmo regulation [34].

The concentrations of zinc and Cu for all the investigated sites were lower than the WHO permissible limit. Naturally, excessive levels of trace metals may be due to geographical processes such as weathering, leaching into rivers through tidal actions. Anthropogenic perturbation contributions of elevated levels of trace metals in marine ecosystem include the following: discharge of untreated industrial waste water, sewage loaded with trace metals, oil spillage and agricultural run-offs, urban, municipal run-offs and marine transportation between farmlands and fishing settlement.

The results for some trace metals in this study were higher than the values reported by Essien et al. [19], who investigated the levels of trace metals in water from Imo River estuary in the Niger Delta. The range for their result in mg/l was as follows: Zn (0.03 - 0.04), Cu (0.01-0.02), Ni (0.003 - 0.01), Pb (0.001- 0.04) and Cd (0.02). Liu et al. [35] observed that all the investigated metals in their study were lower than the permissible limit except Pb. However, the concentration of Fe was the highest which is similar to the findings in this work.

4.1 Health Risk Assessment via Ingestion Pathway

In this study, the target hazard quotient (THQ) via ingestion of water for Pb, Ni and Cd were greater than unity while values for Fe, Zn and Cu were less than unity. This result suggest that Pb, Cd and Ni are the main contributors to non-carcinogenic risk and could have potential health effect such as mild tremor, diabetes, low intelligent quotient etc (by exposure through ingestion of water [24]. The THQ values for Pb, Cd and Ni in this study are higher than values reported by other authors [11,36]. The THQ value for Cd was the highest in the result reported by Essien et al. [19], for water from Imo River estuary in the Niger Delta region of Nigeria. This result is similar to the findings in this study. However, values for THQ in this study were higher than values reported by Maigari et al. [27] and Caylak [24]. The above authors confirmed that values of THQ less than unity suggest ignorable or no significant risk to the local population in the study area.

The risk due to potentially hazardous substances in the same media is assumed to be additive and arithmetic sum of individual THQ is equal to HI [11,37]. In this study, the total target hazard quotient, also known as hazard index (HI) was greater than unity for all the study sites. This indicates that there is a cumulative potential of adverse health risk from cross River estuary via the ingestion of water by the coastal dwellers from the investigated sites.

4.2 Health Risk Assessment via Dermal Pathway

The result from this research revealed that THQ via dermal contact was greater than unity for only Cd at Ebughu. This result is comparable to the findings of Li and Zhang [36] with values for all the investigated trace metals less than unity except for arsenic. In this study the hazard indices via dermal contact was greater than one for all the investigated metals at Ebughu and Ishi et al. the other locations recorded HI values via dermal contact less than one. The result in this study reveals that bathing or showering in water at the control site, Oron and Unyenghe may not pose adverse health effect compared to bathing at Ishiet and Ebughu.

4.3 Source Apportionment And interelement Relationship

Pearson correlation analysis predicts inter relationship between investigated trace metals and identify their possible sources. In this study, Pearson correlation analysis, revealed strong positive correlation between some metals pairs such Cd-Pb, Pb-Fe, Zn-Fe and Cu-Ni. This result indicates that these trace metals might originate from the same pollution source.

Yi et al. [38], reported hat high correlation between specific metals may reflect similar level of contamination or release from same sources of pollution. Mustapha and Aris [39] confirmed that significant positive correlation between metals pair indicate or suggest the possibility of common source or origin.

Inengite et al. [9] reported the use of hierarchical cluster analysis (HCA) for classification in environmental studies into clusters with the use of square Euclidean distance. In this study, two primary clusters were observed in Fig. 2. which predict that nickel might come from a different source compared to other investigated metals. Another cluster was observed between Zn and

Cu and Fe, Pb and Cd. Essien et al. [40] stated that strongly correlated metals indicate strong link between them which probably reflect their related source of origin.

Fig. 3. reveals two clusters with respect to similarities between stations. The control site (Ifiayong) was found in one cluster with the other examined sites in the other cluster. This classification further confirms the fact that the examined sites are close to an industrial site (an oil processing facility) while the control site is far away from an oil processing facility. Further classification involving the three sites namely Oron, Ishiet and Ebughu suggest common pollution source from these sites. Ekpo et al. [41] reported that hierarchical cluster analysis (HCA) was used to extract information about the similarities or dissimilarities among the sampling sites while Etuk [10] used HCA in the classification of sampling location into highly polluted sites and marginally polluted sites.

5. CONCLUSION

Studies on the concentration of some trace metals in water from Cross River estuary (CRE) followed the trend: Ni > Cd > Fe > Pb > Zn > Cu. All the investigated metals were above the WHO stipulated standard in all the locations except Zn and Cu and Fe at the control sites. The target hazard quotients (THQ) via ingestion pathway were greater than unity and the Hazard index was greater than one for all the study sites. The target hazard quotients via dermal contact was less than unity for all the sites except Cd at Ebughu. The hazard indices via dermal pathway were greater than unity at Ebughu and Ishiet. The THQ andhazard indices via ingestion pathway indicate possible cumulative health risk for Pb, Cd and Ni. This call for regular monitoring and management of the risk induced by the above-mentioned trace metals in Cross River estuary.

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COMPETING INTERESTS

Author has declared that no competing interests exist.

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