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ScopeMed

Human Health Risk Assessment of Trace metals in Water from Qua Iboe River Estuary, Ibeno, Nigeria

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ABSTRACT

Aims: This study aimed to determine levels of trace metals in Qua Iboe river estuary (QIRE), Ibeno and estimate human health risk associated with water from the river via ingestion and dermal exposure. **Method:** Trace metals in water from QIRE was measured using atomic absorption spectrophotometer and human health risk induced by the trace metals in dry and wet seasons was investigated using mathematical models recommended by United States Environmental Potential Agency (USEPA). **Results:** The range for the different metals investigated in dry season were as follows: Pb (0.147 to 0.19mg/l), Cd (0.02 to 0.31mg/l), V(0.04 to 0.11mg/l), Cr (0.09 to 0.18mg/l), Ni (0.28 to 0.61mg/l), Fe (8.78 to 13.97mg/l), Zn (0.13 to 0.56mg/l). The results for wet season were: Pb (0.07 to 0.19mg/l), Cd (0.05 to 0.31mg/l), V (0.01 to 0.03mg/l), Cr (0.02 to 0.15mg/l), Ni (0.03 to 2.33mg/l), Fe (0.02 to 4.92mg/l), Zn (0.11 to 0.43mg/l). Concentrations of metals were above USEPA limits except Zn. The target hazard quotient (THQ) and hazard index (HI) values via ingestion of water were greater than one while the THQ values via dermal contact were greater than one for Cd only. The combined target hazard index (HI*) from ingestion and dermal contact of water was greater than unity for Cd, Cr and Pb for wet and dry seasons. **Conclusion:** Findings in this study show that Pb, Cd and Cr may contribute to health risk from dermal and oral exposure to water from the QIRE systems. Constant monitoring and remediation processes of the QIRE are strongly recommended.

KEY WORDS: Risk assessment, trace metals, hazard index, Qua Iboe river estuary, Nigeria

INTRODUCTION

Water pollution occurs when the quality of the water is altered in a way that affects either the organisms living in the water or suitability of the water for domestic use such as swimming, irrigation and drinking. According to [1] water is polluted when foreign substances are added to it and this deteriorates the quality of water. Trace metals are elements that occur at very low levels of a few parts per million or less in a given system [2]. They occur as dissolved or particulate trace metals in marine environment. They are classified as essential and non-essential (toxic) metals based on their importance to the human body [3].

Lifetime exposure to contaminants such as trace metals and other chemicals in the environment through ingestion, inhalation and dermal contact can pose risk to human health. Human health risk process is used to estimate the nature and probability of adverse health effect in humans exposed to contaminants in environmental media, in the immediate or in the nearest future [4]. The risk assessment evaluates the consequences of human activities and weighs the adverse effect to public health against the contribution to economic development. Risk assessment procedures are based on source-pathway-receptor models and it involves the examination of site characteristics, environmental behaviour and toxicity of the contaminant, its potential route of entry into the receptor (humans), exposure of the receptors to the contaminants and their response to the dose [5]. Generally, risk assessment has been used by risk managers to link scientific information provided by a risk assessor about potentially hazardous substance for decision making. One of the priorities of sustainable development involves assessment and management of risk due to exposure to contaminants such as trace metals (6).

Human health risk associated with the consumption of contaminated water have been investigated in other studies [7,8,9]. All the water samples investigated had the potential of carcinogenic and non-carcinogenic risks on the consumers.

The activities of oil industries in the Niger Delta region of Nigeria has impacted negatively on surface water quality around the area resulting in the release of large amounts of hydrocarbons and trace metals into the terrestrial and aquatic environment. This has led to disruption of socio-economic activities, water scarcity and poor aesthetics of most water bodies [10,11]. Ibeno located in the Niger Delta region of Nigeria, is a large fishing settlement located along the lower reach of Qua Iboe river estuary (QIRE). Other than fishing, the water from the area is also used for irrigation and domestic purposes. In some settlements, the river serves as a source of drinking water and for recreational activities such as swimming. Domestic wastes are also discharged from homes into the river and industrial effluents from a petrochemical plant located in the area are emptied into the water source.

Studies on trace metals concentration in QIRE and its associated creeks have been carried out by researchers [12,13,14]. However, there is little or no data available on the health risk assessment of trace metal contamination of water from the estuary. This study seeks to investigate the levels of trace metals in Qua Iboe river estuary (QIRE), Ibeno-Nigeria and estimate human health risk associated with water from the river via ingestion and dermal exposure.

MATERIALS AND METHODS

Study Area

The study area is located in the lower reach of Qua Iboe river estuary (QIRE) in Ibeno local government area of Akwa Ibom State, Niger Delta region of Nigeria, where petroleum exploration activities by oil companies abound. The five sampling (examined) sites selected for the study were: Okoroutip (4°55’5’’N 7°54’47’’E), Ukpenekang (4°27’2’’N 8°3’5’’E), Iwochang (4°36’50’’N 7°50’51’’E), Douglas creek (4°30’55’’N 8°07’E) and Stubb creek (4°34’41’’N 7°59’47’’E). Ekpene Ukpa (4°47’90’’N 7°50’03’’E) located about 20 km from the other sites and free from oil exploration activities, was selected to serve as the control site. Wet (rainy) and dry seasons exist in the study area. The mean annual rainfall ranges between 2000 to 3000mm (15). Fig 1 shows a map of the study area indicating the sampling sites.

Samples and sampling

Surface water samples were collected from the selected locations with a 500ml sterilized polyethylene bottle according to the method of [16]. Sampling was conducted monthly from November, 2013 to October, 2014. The samples from six points per sampling site 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 analyses.

Determination of trace metals

Digestion of the water samples was performed as described by [17]. After appropriate digestion, the trace metals were determined using atomic absorption spectrophotometer (Unicam, 939/959 model). All analyses were performed 3days after each sampling.

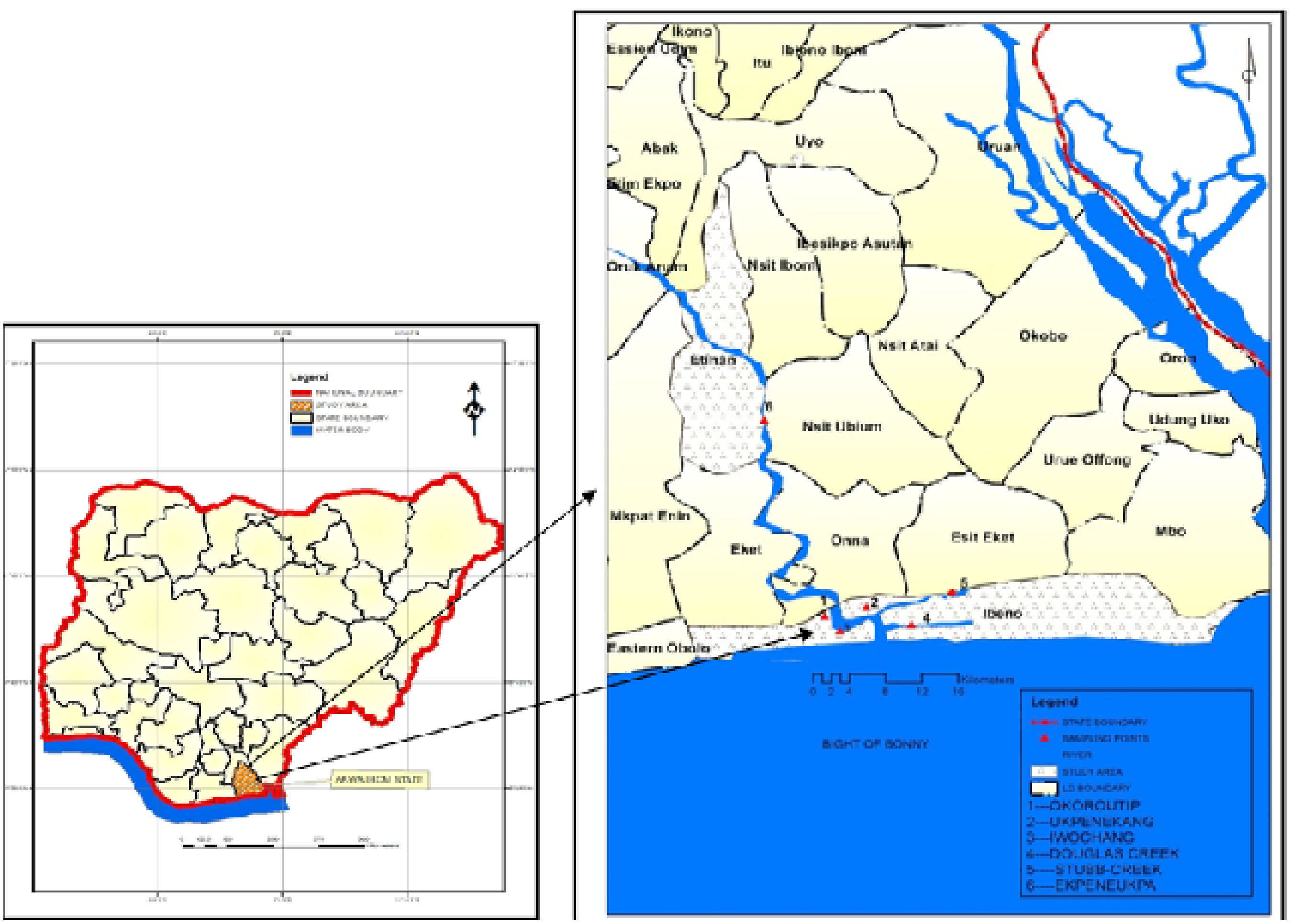


Figure 1. Map of Akwa Ibom State, Nigeria showing the study locations and sampling sites at Ibeno (see arrows)

The trace metals were determined using atomic absorption spectrophotometer (Unicam, 939/959 model). Before the determination of any sample, a calibration curve was prepared using aliquots from standard stock solution of the metal. The working standards prepared by dilution of the stock solution. This was used for the calibration of the spectrophotometer. A hallow cathode lamp for each metal was used for the calibration of the instrument using the working standard solutions. Each of the working standards was sprayed or aspirated into the flame and the corresponding absorbance for each concentration recorded. A blank was similarly determined.

Statistical analysis

All values were expressed as mean ± SD. Students t – test was used to compare between means and a *P*<0.05 was considered statistically significant. Statistical analyses were performed using SPSS statistics 16.0 for windows (Chicago, 2007).

Non-carcinogenic risk assessment

Non-carcinogenic risk of some trace metals in water was predicted from their target hazard quotient (THQ) and hazard index (HI) indices obtained from the equation predicted by [18,19].

The potential exposure pathways of metal in marine environment are through ingestion and dermal contact. Exposure doses through ingestion and dermal pathways were calculated by the following equations [20].

Average daily intake via ingestion were calculated by equation 1

$$ADIi = \frac{C \ x \ IR \ x \ EF \ x \ ED}{Bw \ x \ AT} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

[where ADI*i* is the average daily intake via ingestion (mg/kg -day), C is the concentration of the chemical, IR is the intake rate (2L per day for water), BW is the body weight of the exposed person (70kg for normal adult), EF is the exposure frequency (365days/ year), ED is the exposure duration over a life time (70 years), AT is the averaging time in days (70 years x 365 days/year)].

Average daily intake via dermal pathway were calculated by equation 2

$$ADId = \frac{C \ x \ EF \ x \ ED \ x \ SA \ x \ Kp \ x \ ET}{Bw \ x \ AT} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

[where ADI*d* is the average daily intake via dermal pathway (mg/kg -day), C is the concentration of the metal in water (mg/l), SA is the drinking water exposed skin area (cm^2) =28000, Kp is the dermal permeability coefficient (cm/hr), ET is the exposure time during bathing and shower (hr/day) =0.6 EF is the exposure frequency (days/year)=365, ED is the exposure duration (year)= 70years, BW is body weight (kg) = 70kg, AT is the averaging time (days) = 25550days, CF is the unit conversion factor (L/cm^3) = 0.001

Target hazard quotient for oral THQ*i* route was calculated as

$$THQi = \frac{ADIi}{RFD} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

RfD = oral reference dose of the contaminant (mg /kg/ day).

Target hazard quotient for dermal pathway THQ*d* route was calculated as

$$THQd = \frac{ADId}{RfDdermal} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

RfD dermal = dermal reference dose of the contaminant (mg /kg/day).

$$HI^* = THQi + THQd \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

HI* =Sum of THQ from ingestion and dermal pathway.

$$HI = THQ(toxicant\ 1) + THQ\ (toxicant\ 2) + \cdots \ldots\ldots\ldots . + THQ(toxicant\ n) \ldots\ldots\ldots (6)$$

In this case, the hazard index HI or total THQ is treated as the arithmetic sum of the individual metal THQ values [21].

RESULTS

The concentrations of trace metals in the water from QIRE, sampled from six locations for the dry season are presented in Table 1. The average concentration of the trace metals for the dry season ranged between 0.38 mg/l for Zn and 11.31 mg/l for Fe and the trend for metal concentration was Fe>Ni>Zn>Cd = Pb>Cr>V. The coefficient of variation from the stations had values ranging from 2.3 to 21.0 % for Pb; 12.5 to 18.1% for V; 2.6 to 30.9 for Fe. Higher variability 15.0 to 77.4% were measured for Cd at most of the stations except Okoroutip. Coefficient of variation was highest (15.5 to 71.4%) at Ekpene Ukpa (the control site) when compared with examined sites. The concentrations of trace metals in QIRE at the six locations sampled in the wet season are presented in Table 2. Average concentrations for trace metals measured at the stations ranged between 0.14+0.02 - 0.19+0.02mg/l for Pb and 2.23+0.30 – 4.92+0.50mg/l for Fe. The values in the wet season decreased according to the following trend: Fe>Ni>Zn>Cd>Pb = Cr >V. The mean concentrations recorded for the dry season were significantly higher (P<0.05) than that obtained for the wet season.

Table 1. Trace metal concentration in water from Qua Iboe River Estuary (QIRE) during the dry season in mg/l

Location	Pb		Cd		V		Cr		Ni		Fe		Zn	
	Mean	CV (%)	Mean	CV (%)	Mean	CV (%)	Mean	CV (%)	Mean	CV (%)	Mean	CV (%)	Mean	CV (%)
Okoroutip	0.17±0.01	2.30	0.02±0.003	15.0	0.11±0.02	18.1	0.18±0.08	44.4	0.41±0.13	31.7	10.59±3.28	30.9	0.59±0.13	22.0
Ukpenekang	0.19±0.01	5.26	0.13±0.10	76.9	0.06±0.01	16.6	0.12±0.03	41.7	0.38±0.20	52.6	10.67±1.55	14.5	0.13±0.04	30.7
Iwochang	0.14±0.02	14.2	0.17±0.06	35.2	0.05±0.01	20.0	0.13±0.05	38.5	0.51±0.008	15.6	11.38±2.82	24.7	0.56±0.07	12.5
Douglas Creek	0.19±0.04	21.0	0.31±0.24	77.4	0.05±0.01	18.0	0.12±0.06	50.0	0.53±0.08	15.0	12.51±1.71	13.7	0.36±0.06	16.7
Stubb Creek	0.15±0.02	13.3	0.24±0.08	33.3	0.08±0.01	12.5	0.13±0.06	46.1	0.61±0.13	21.3	13.97±0.37	2.6	0.31±0.08	25.8
Ekpene Ukpa (control)	0.07±0.05	71.0	0.03±0.02	66.6	0.04±0.01	25.0	0.09±0.06	66.6	0.28±0.16	57.0	8.78±0.76	8.6	0.33±0.05	15.5
Average	0.15		0.15		0.07		0.13		0.45		11.31		0.38	
WHO value	0.05		0.05		0.05		0.05		0.02		0.3		3	
FEPA value	0.05		0.01				0.06		0.01		0.3		5	

Table 2. Trace metal concentration in water from Qua Iboe River Estuary (QIRE) during the wet season in mg/l

Location	Pb		Cd		V		Cr		Ni		Fe		Zn	
	Mean	CV (%)	Mean	CV (%)	Mean	CV (%)	Mean	CV (%)	Mean	CV (%)	Mean	CV (%)	Mean	CV (%)
Okoroutip	0.08±0.02	25.00	0.13±0.01	7.69	0.02±0.01	50.00	0.13±0.01	7.69	0.421±0.06	14.30	2.23±0.30	13.45	0.34±0.03	8.82
Ukpenekang	0.19±0.02	10.50	0.11±0.01	9.09	0.03±0.01	33.30	0.13±0.007	5.38	0.33±0.04	12.10	3.68±0.34	9.23	0.17±0.03	17.60
Iwoachang	0.08±0.01	12.50	0.14±0.01	7.14	0.03±0.02	66.60	0.12±0.03	25.00	0.32±0.004	12.50	3.98±0.84	21.10	0.43±0.05	11.60
Douglas Creek	0.11±0.01	9.09	0.20±0.02	10.00	0.03±0.04	13.30	0.15±0.004	2.60	2.33±0.78	96.30	3.54±0.64	18.00	0.46±0.05	10.80
Stubb Creek	0.07±0.01	14.20	0.20±0.02	10.00	0.02±0.01	50.00	0.10±0.05	5.00	0.47±0.05	10.60	4.92±0.50	10.10	0.11±0.07	36.30
Ekpene Ukpa (control)	0.10±0.02	20.00	0.05±0.003	60.00	0.010±0.008	80.00	0.02±0.01	50.00	0.03±0.01	33.30	0.028±0.02	71.40	0.16±0.08	50.00
Average	0.11		0.13		0.02		0.11		0.65		3.06		0.27	
WHO value	0.05		0.05		0.05		0.05		0.02		0.3		3	
FEPA value	0.05		0.01				0.06		0.01		0.3		5	

Health Risk Assessment via Ingestion of Water

The levels of target hazard quotient (THQ) of selected trace metals in water from QIRE during the dry season are summarized in Table 3. THQ values are between 1.00 and 1.05 for Pb, 0.60 and 9.0 for Cd, 0.15 and 0.33 for V, 1.14 and 1.73 for Cr, 0.55 and 0.87 for Ni, 0.36 and 0.57 for Fe, and 0.01 and 0.06 for Zn. THQ values for the control station for all the trace metals were between 0.11 and 0.83. The decrease in the level of THQ during the dry season followed the order: Cd > Cr >Pb> Ni > Fe > V > Zn. The percentage contributions from different trace metals to HI followed the trend: Cd > Cr > Ni >Pb> Fe > V > Zn. The levels of target hazard quotient (THQ) of selected trace metals in water from QIRE during the dry season are summarized in Table 4. THQ values are between 0.50 and 1.35 for Pb, 3.14 and 5.71 for Cd, 0.06 and 0.10 for V, 0.95 and 1.71 for Cr, 0.46 and 0.67 for Ni, 0.09 and 0.20 for Fe, and 0.01 and 0.04 for Zn. THQ values for the control station for all the trace metals were between 0.01 and 0.71. The decrease in the level of THQ during the wet season followed the order: Cd > Cr >Pb> Ni > Fe > V > Zn

Health risk assessment via dermal contact of the water

The level of THQ via dermal exposure route is summarized in Tables 5 and 6 for both seasons and the values decreased according to the order: Cd > Cr >Pb> V > Ni > Fe>Zn, for both seasons. Generally the THQdermal values were all below unity (<1) for all the measured metals at the various stations, except for Cd which had THQdermal values greater than one. The reference oral dose and dermal permeability coefficients for trace metals are shown in Table 7.

Hazard index for combined pathways in wet and dry seasons

The hazard index for combined pathways in wet and dry seasons are shown in Figures 2 and 3 respectively. Douglas and Stubb creeks located close to a petroleum processing plant recorded the highest value for Cd for both seasons while Zn had the lowest values. In a decreasing order the concentrations were: Cd>Cr>Pb>Ni>Fe>V>Zn for both seasons.

Table 3. Target hazard quotient and hazard index of trace metals via ingestion of water from QIRE during the dry season

Location	Pb	Cd	V	Cr	Ni	Fe	Zn	HI
Okoroutip	1.20	0.60	0.33	1.73	0.60	0.43	0.06	4.95
Ukpenekang	1.25	4.00	0.22	1.14	0.55	0.43	0.01	7.60
Iwoachang	1.00	5.00	0.15	1.23	0.73	0.46	0.05	8.62
Douglas Creek	1.35	9.00	0.16	1.14	0.76	0.51	0.03	12.95
Stubb Creek	1.05	7.00	0.33	1.24	0.87	0.57	0.02	11.08
Ekpene Ukpa (control)	0.50	0.80	0.11	0.83	0.40	0.36	0.03	3.03
Relative contribution to HI (%)	13.16	54.73	2.69	15.16	8.11	5.72	0.41	

Table 4. Target hazard quotient and hazard index of trace metals via ingestion of water from QIRE during the wet season

Location	Pb	Cd	V	Cr	Ni	Fe	Zn	HI
Okoroutip	0.55	3.71	0.06	1.23	0.60	0.09	0.03	6.28
Ukpenekang	1.35	3.14	0.10	1.23	0.47	0.15	0.02	6.60
Iwoachang	0.55	4.00	0.09	1.71	0.46	0.16	0.04	7.02
Douglas Creek	0.78	5.71	0.10	1.43	3.33	0.14	0.04	11.53
Stubb Creek	0.50	5.71	0.06	0.95	0.67	0.20	0.01	8.11
Ekpene Ukpa (control)	0.71	0.14	0.03	0.17	0.04	0.01	0.02	1.13
Relative contribution to HI(%)	10.91	55.10	1.08	16.52	13.69	1.844	0.393	

Table 5: Target hazard quotient of trace metals in water from QIRE via dermal pathway during the dry season

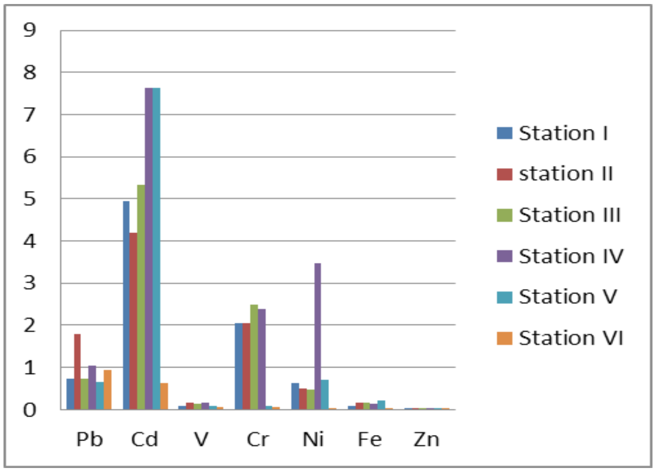
Location	Pb	Cd	V	Cr	Ni	Fe	Zn
Okoroutip	0.3885	0.1920	0.2030	1.1520	0.0246	0.0182	0.0014
Ukpenekang	0.4342	1.1248	0.1028	0.7681	0.0228	0.0183	0.0003
Iwoachang	0.3200	1.6320	0.0923	0.8320	0.0306	0.0195	0.0013
Douglas Creek	0.4342	2.9760	0.0923	0.7681	0.0318	0.0214	0.0008
Stubb Creek	0.3428	2.0161	0.1476	0.8320	0.0366	0.0239	0.0007
Ekpene Ukpa (Control)	0.1600	0.2880	0.0738	0.5760	0.0168	0.0150	0.0008

Table 6. Target hazard quotient of trace metals in water from QIRE via dermal pathway during the wet season.

Location	Pb	Cd	V	Cr	Ni	Fe	Zn
Okoroutip	0.1828	1.2480	0.0369	0.8320	0.0252	0.0038	0.0008
Ukpenekang	0.4342	1.0560	0.0554	0.8320	0.0198	0.0063	0.0004
Iwoachang	0.1828	1.3440	0.0544	0.7680	0.0192	0.0068	0.0010
Douglas Creek	0.2514	1.9200	0.0554	0.9600	0.1398	0.0061	0.0011
Stubb Creek	0.1600	1.9200	0.0369	0.6400	0.0282	0.0084	0.0003
Ekpene Ukpa (Control)	0.2285	0.4800	0.0185	0.1280	0.0018	0.0001	0.0004

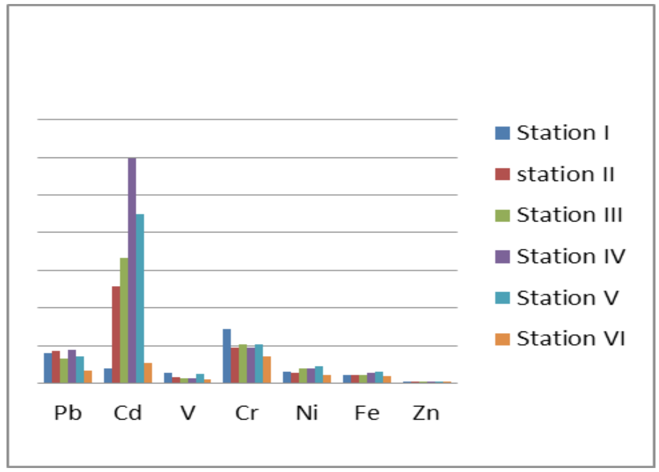
Table 7. Reference dose and dermal permeability coefficient for the investigated trace metals [19]

Reference dose	Pb	Cd	V	Cr	Ni	Fe	Zn
Oral reference dose (mg/kg/day)	4.0×10^{-3}	1.0×10^{-3}	9.0×10^{-3}	3.0×10^{-3}	2.0×10^{-2}	7.0×10^{-1}	3.0×10^{-1}
Dermal reference dose (mg/kg/day)	4.2×10^{-4}	2.5×10^{-5}	1.3×10^{-4}	7.5×10^{-5}	8.0×10^{-4}	1.4×10^{-1}	6.0×10^{-2}
Dermal permeability coefficient (cm/hr)	1.3×10^{-4}	1.0×10^{-3}	1.0×10^{-3}	2.0×10^{-3}	2.0×10^{-4}	1.0×10^{-3}	6.0×10^{-4}



Key: Stations I: Okoroutip; II:Ukpenekang; III: Iwoachang; IV: Douglas Creek; V: Stubb Creek; VI: Ekpene Ukpa (control site

Figure 2: Hazard index for combined pathways in the wet season



Key: Stations I: Okoroutip; II:Ukpenekang; III: Iwoachang; IV: Douglas Creek; V: Stubb Creek; VI:Ekpene Ukpa (control site

Figure 3: Hazard index for combined pathways in the dry season

DISCUSSION

The findings in this study revealed that Fe, Pb and Zn were concentrated significantly at the sampled stations in the dry season. The concentration of lead, cadmium and vanadium in this study are comparable to the values reported by [22] while that of iron are comparable to the values reported by [13] for water from Stubb Creek. Research by [23,24] showed lower values for the same trace metals investigated. In contrast to other investigated metals, the concentration of nickel was higher in the rainy season than the dry season. This is consistent with the results of studies by [11,23].

The concentration of all the metals exceeded the stipulated standards of World Health Organization [27], Standard Organization of Nigeria [28] and Federal Environmental Protection Agency [29] with the exception of Zn. The higher level of trace metals in dry season compared to rainy season has been linked with factors such as mechanism of deposition, transport of solute compounds during the rainy season, ion exchange of metals with sea-salt cations which reduces metals concentration in rainy season and the growth of aquatic organisms in the rainy seasons unto which metals can cling [22].

In this study, the average level of lead in dry season was higher than the level in the rainy season. The high level of lead in dry season may be due to evapo-crystallisation process and low precipitation signifying low dilution. Otitoju and Otitoju [30] reported that lead in marine environment is associated with oil exploration, pipeline transportation, corrosion inhibition as well as other processes. Exposure to lead has been implicated as the reason for some learning disorders observed in children [31]. Also, concentration of lead in human body above permissible limit is capable of inducing abdominal pains, vomiting, drowsiness, anaemia, convulsion and malfunctioning of the kidney, pancreas, brain and reproductive system. Long term exposure to Cd from water causes kidney dysfunction, loss of calcium from the bone resulting in osteoporosis and osteomalacia [32]. Also, it has been reported that acute neurological effect of Cd toxicity could manifest as nausea, abdominal cramp, bloody diarrhoea, chest pain and dizziness [1]. The average value of Cd in both dry and wet seasons was five times higher than the permissible limit proposed by [27]. The level of Cd in this study is compared with findings in other locations although in some cases low and high values were reported compared to values obtained in this study [33,34].

The control site in this study (Ekpene Ukpa) had the lowest value for the metals measured, while Douglas and Stubb creeks located close to a petroleum processing plant recorded the highest value especially during wet seasons. According to [13] nickel can be introduced into the ecosystem during drilling or oil spillage. Nickel toxicity has been linked with cancer of the lungs, nose, and bone and skin irritation [23] while Cr toxicity can result in cancer of the lungs and kidney [1].

The high level of iron (8.6mg/l) in the control site during the dry season indicates that the source of iron in the marine ecosystem may not just be due to oil exploration and exploitation activities. Iron is the second most abundant metal in the earth crust [23]. High levels of iron in sediment and water samples may be due to the discharge of iron-laden wastes and effluents replete with corroded iron pipes, containers and scraps into the water body. Chronic consumption of water with iron overload (above 0.3mg/l) results in gene mutation resulting in haemochromatosis with symptoms such as fatigue, weight loss, joint pains, liver and heart disease. Other health effects include severe allergic reactions such as rash, itching, streaks of blood in stools, vomiting and stomach pains [35].

Generally, agricultural drainage water from pesticides and fertilizers, industrial effluents and run-offs in addition to sewage are responsible for large amounts of inorganic anions and trace metals introduced into the marine environment. Other anthropogenic sources of trace metals include oil spillage, domestic waste, atmospheric deposition and emission from fossil fuel burning etc [36]. Also, cadmium coating are good anticorrosive agent in marine environment, if corroded or damaged cadmium may be introduced into the environment. Nwajei [37] reported that cadmium is a pollutant in detergents, sewage, phosphate fertilizers and refined petroleum product while [38] listed sources of cadmium in the marine ecosystem to include waste from cadmium based batteries, run-offs from agricultural soils where phosphates are used as fertilizers. Nickel, iron and vanadium are trace metallic components of crude oil that occur as metalloporphyrin, transition metal complexes or organometallic compounds and the ratio of vanadium/ nickel have been used to differentiate crude oil from various locations [39].

Coefficient of variation (CV) is the measure of the variability of the data; when it is higher, it means the metals at the control site have higher variability and less stability. The CV is a statistical measure of the distribution of data points in a data series around the mean. CV helps to compare the degree of variation of one data series to another [23] reported that the values of CV in an environmental medium give an indication of the distribution of the pollutants and its degree of variability. According to Udosen et al. [13], the lower the CV of a trace metal in an environmental sample, the more stable the trace metal. More stable metals have the ability of persisting in the environment and this may result in higher pollution level bioaccumulation. Sheelan and Muller [24] studied the level of pollution in samples from three streams. The CV was low for samples from grossly polluted streams and increased in value for stations that are progressively less polluted.

Health Risk Assessment via Ingestion of Water from QIRE

The calculated THQ values in this study for Fe, Zn, V, and Ni at QIRE were less than unity while values for Pb, Cd, Cr were greater than unity. This result suggests that Pb, Cd and Cr are the main contributors to non-carcinogenic risk exposure via ingestion of water from QIRE. The THQ ingestion values in this study are similar to those reported by [35], higher than values reported by [40] and lower than values reported by [41]. Li and Zhang [42] reported values for THQ for some metals that ranged from 1.06E – 04 to 9.32E-01 and their HI values ranging from 6.862E – 04 to 9.76E-01 in water from Upper Han river in China. The HI values reported by [35] ranged from 0.25 to 156.22 while [40] reported HI values that were less than unity for drinking water in the Kohistan region of Pakistan.

The THQ values calculated for Pb, Cd and Cr show that these metals could have potential health effect relating to non-cancer diseases such as low intelligent quotient, mild tremor, diabetes etc. [17,18]. The toxic risk due to potentially hazardous substances in the same media is assumed to be additive and the arithmetic sum of individual THQ is equal to HI [19, 43, 44]. In this study, the total hazard index (HI) was greater than unity for all the locations in both dry and wet seasons. This indicates that there is a cumulative potential of adverse health risk in the water samples from QIRE via direct ingestion by the inhabitants of the locations under study.

Health risk assessment via dermal contact with QIRE water

The results of this study revealed that THQ for dermal contact was greater than one for Cd at Ukpenekang, Iwochang, Douglas creek and Stubb creek and Cr at Okoroutip during the dry season. However, in the wet season, THQ for Cd was greater than one in all the study sites. Values of THQ dermal reported by Li and Zhang [42] for trace metals in water from Upper Han River were less than one except for arsenic. In their study, the hazard indices for the ingestion and dermal contact of water was greater than one for Pb, Cr, and Cd and less than one for other metals. The findings in this study compared favourably with that from the Upper Han River study. The results in this study further revealed that showering or bathing in water at the control station (Ekpene Ukpa) where lower THQ values were obtained may not pose adverse health effect compared to water at the examined stations. According to Caylak [18], when the sum of THQ from applicable pathway is greater than one, there may be potential adverse effect on human health. Findings in this study therefore indicate that Pb, Cd and Cr are the major contributors to non-carcinogenic health risk from dermal and ingestion pathways for both wet and dry seasons.

CONCLUSION

The trace metals present in water from QIRE followed the trend Fe > Zn > Ni > Cd >Pb> Cr > V and when compared with international standards, all the metals investigated were above the permissible limit except Zn. The target hazard quotient (THQ) via ingestion route and the total target quotients for all the metals (Hazard Index) were above unity indicating possible non-carcinogenic adverse health effect. The THQ values via dermal contact indicated possible risk due to Cd observed in all the stations and at all seasons, whereas the risk due to Cr was observed at Okoroutip only in the dry season. However, the combined risk assessment for water and dermal contact pathways (HI*) was more than unity for Cd, Cr and Pb, indicating cumulative health risks that may emanate from these metals through dermal contact or ingestion of QIRE water. Constant monitoring and remediation processes of the QIRE are strongly recommended.

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