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Toxicological Evaluation of Contamination by Potentially Toxic Elements (PTEs) and Related Risks in the Surface Waters of Three Tidal Streams of the Niger Delta, Nigeria

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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ABSTRACT

This work investigated the physicochemical parameters and potentially toxic elements (PTEs) in the surface water samples collected from three tidal streams (Bonny, Krakrama and Buguma) in the Niger Delta, Nigeria. Potentially toxic elements such as arsenic (As), boron (B), cadmium (Cd), cobalt, (Co), chromium (Cr), lead (Pb), nickel (Ni) and selenium (Se) were analysed using atomic absorption spectrophotometer. Physicochemical parameters were evaluated in situ using portable instruments and also in the laboratory. These parameters and PTEs were used to compute the water quality index, comprehensive pollution index, pollution load index, metal evaluation index, and toxicity load index. The ecological and health risks were also analysed. The PTEs found in the water samples were higher than the acceptable limit by WHO standards and followed the trend of Ni

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> Pb > Cr > Co > Se > As > Cd > B. Nickel was the most abundant element in water with the maximal concentration of 5510 µg L^{-1}. The calculated contamination indices concluded that the streams were extensively polluted. Based on the permissible toxicity loads, maximum of 99%, 100%, 98%, 98%, 100%, 99%, and 97% of As, Cd, Co, Cr, Pb, Ni and Se respectively should be removed from the surface water of the streams in the Niger Delta to address safety and health. The PTEs in water exerted very high ecological risks. Overall, the estimated lifetime cancer risk of PTEs due to ingestion of water at Bonny, Krakrama and Buguma streams were 5.72×10^{-3}, 2.88×10^{-3} and 2.3×10^{-3} respectively. The results guide controlling the PTE pollution and important information on PTEs for the formulation of the necessary remediation policies to improve water quality and protect the human health of dwellers along the Niger Delta.

Keywords: Surface water; potentially toxic elements; water quality index; toxicity load; hazard intensity; ecological risk; health risk.

1. INTRODUCTION

The earth is said to be made entirely of water, and surface water serves as a vital source of support for both aquatic and terrestrial life [1]. Surface water quality is a very vital factor concerning aquatic ecosystems and human health [2]. Urban and industrial wastewater discharge, sudden increases in anthropogenic and human development activities, and water quality degradation are all serious concerns as they endanger the viability of the aquatic ecosystem [3]. Potentially toxic elements are naturally occurring constituents of the earth's crust and ubiquitous chemically stable substances. Many elements are indispensable to living organisms but some of them are noxious at high concentrations; these include boron (B), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), selenium (Se) and zinc (Zn). Other elements such as arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb) and nickel (Ni) are toxic to living organisms even at low concentrations [4], and are listed among the eight most common and widespread PTEs in the environment concentrations [5]. Aquatic ecosystem contamination by PTEs has attracted global attention in recent years and are considered priority pollutants in the water environment due to their long retention, high toxicity, non-biodegradability and bioaccumulation tendency, and persistence potentials, and deleterious effects on living organisms including humans [6,7,8].

Toxic elements may enter the human body via drinking water or indirectly via the food chain, posing a potential threat to human health. The PTEs may come from both natural sources (e.g., bedrock erosion, chemical weathering and leaching) and anthropogenic activities (e.g., mining, mineral processing, industrial wastewater, manufacturing and agricultural production, the application of pesticides and fertilizers) [9]. The released PTEs may enter the aquatic ecosystem mainly through two routes; the direct discharge pathways (e.g. municipal/industrial effluents, sewage discharges, water transport, accidental oil leakages and surface runoff) and indirect sources (e.g., atmospheric dry/wet deposition, air-sea gas exchange) [10,11] and lead to PTE pollution of the aquatic ecosystem.

These PTEs are carcinogenic, teratogenic and endocrine disruptors even at low concentrations; some others cause neurological and neurodegenerative diseases and behavioural changes in human beings [12] and are classified as priority elements that are of great public health significance and adverse health effect to all forms of life [13]. PTEs that surpass accepted standards can pose a high risk to ecosystems due to their indefatigable biogeochemical effects, ecological impacts, and bio-accumulative and non-biodegradable nature. The use of contaminated water has health effects and if people use it for a long time, then various types of acute and chronic health problems occur. PTEs are pluripotential and long-term exposure to them is associated with a range of adverse health effects. Chronic exposure to inorganic As promotes the development of some cancers which include cancers of the skin, bladder, lung, liver (angiosarcoma), kidney and possibly colon; neurological, gastrointestinal, haematological and birth disorders, diabetes, peripheral vascular and cardiovascular diseases [14,15]. According to WHO [16], other adverse health effects that may be associated with long-term ingestion of inorganic arsenic include Blackfoot disease, increases in mortality in young adults, and negative impacts on cognitive development, intelligence, and memory. Long-term ingestion of Cd increases the risk of various cancer, including breast, lung, prostate, nasopharynx, bone marrow, pancreas, and kidney cancers, as well as linked to reproductive failure; DNA damage, bone defects (osteomalacia and osteoporosis), increased blood pressure and hypertension [17,18]. Chronic exposure to Cr(VI) is related to kidney, liver, circulatory and nerve tissue damage, reproductive and developmental problems, bronchial asthma, skin allergies, lung and nasal ulcers and cancers [19]. Long-term Ni consumption has been associated with damage to the nervous system and DNA, cardiovascular and kidney diseases, epigenetic effects, bronchial asthma and inflammation as well as systemic toxicity [20,21]. Harmful health effects due to chronic Pb consumption include severe damage to the human central nervous system and reproductive system, haematological damage, skeletal haematopoietic capacity problems, renal failure, cerebral impairment, enzymatic inhibition, retardation of cognitive development and IQ in children, gastrointestinal damage, metabolic poison, as well as pregnancy complications and even death [14,22,23,24].

In this present study, we chose the streams of Buguma, Krakrama and Bonny, and collected some surface water samples from these areas. The objectives of this study were therefore (1) to determine the concentrations of PTEs in surface water samples of the streams, (2) to assess the contamination status using the water quality index (WQI), comprehensive pollution index, pollution load index, PTE evaluation index (PEI), and toxicity load of PTEs to predict the PTE toxicity load the necessary removal of the PTEs from the water bodies to make it safe for human use, and (3) and to appraise the ecological and human health risks posed by the target PTEs in surface waters using carcinogenic risk index based on USEPA risk model. The results of this work can be applied to give new insights into the pollution status of PTEs and thereby facilitate both the development of appropriate strategies/ecological remediation to increase water management efficiency in nearby areas and similar riverine systems to protect aquatic organisms as well as prevent hazards of PTE contamination of its consumers.

2. MATERIALS AND METHODS

2.1 Study Area Description

Buguma stream is located in Asari Toru Local Government Area of Rivers State, Nigeria. It is situated between longitude 6° 51' 44.50" E and latitude 4° 44' 10.10" N. Krakrama stream is located in Asari Toru Local Government Area of Rivers State, Nigeria and lies between longitudes 6°57'03.0"E latitude 4°33'04.0"N. Bonny stream is located in Bonny Local Government Area of Rivers State, Nigeria. It lies between Longitude 7° 05' 60.00" E and Latitude: 4° 22' 59.99" N (Fig. 1). These tidal streams serve as water for domestic purposes and transportation, and receive industrial effluents and wastes from illegal artisan refineries all year round.

2.2 Sample Collection

Water samples from each of the streams were collected into 2500 mL amber glass bottles with Teflon-lined tops and sealed with Teflon tape. For each stream, water samples were collected from three different sampling locations. The samples were properly labelled for identification of sources, stored in an ice-packed cooler at 4°C and immediately transported to the laboratory as soon as after sampling for preservation and analysis. The duration of preservation of the water samples was seven days at a temperature of 4^oC (in a fridge) by adding HNO_3 to maintain a pH < 2, according to the industrial waste resource guidelines [26].

2.3 Sample Preparation and Analysis

2.3.1 Physicochemical analysis, sample collection, pre-treatment, and extraction

The analysis was carried out for various water quality parameters using the standards, protocols and methods described by APHA [27]. Physicochemical analysis carried out for surface water samples includes hydrogen ion concentration (pH), temperature, electrical conductivity (EC), turbidity, total alkalinity, dissolved oxygen (DO), total dissolved solids (TDS), chemical oxygen demand (COD) and biochemical oxygen demand (BOD). The pH, temperature, electrical conductivity, total dissolved solids (TDS) and turbidity of water samples were measured on-site using a portable pH meter (HI-99130, Italy), a mercury-in-glass thermometer calibrated in degree Celsius, conductivity meter (JENWAY, multi-3410, UK), TDS meter (JENWAY– 430) and turbidity meter (SGZ 200BS Turbidity Meter) respectively. Dissolved oxygen (DO) and biological oxygen demand (BOD) were done using the titrimetric method (Wrinkler) as clearly described by Dubey and Maheshwari [28]. Other physicochemical

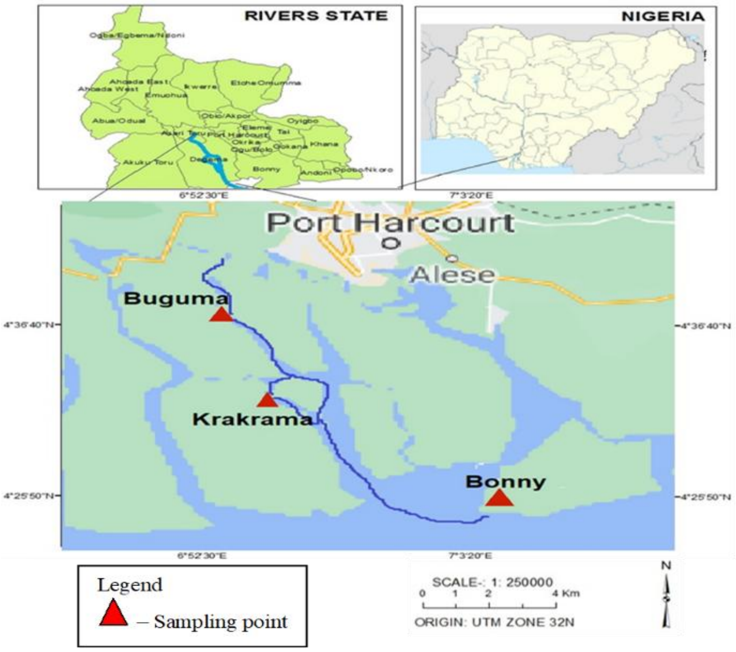

Fig. 1. Map showing the study area [25]

variables were measured based on the procedures described in APHA [27]. Each analysis was carried out in triplicate, and the mean value was adopted. The instruments were calibrated following the manufacturers' guidelines before taking the measurements. The value of each sample was taken after submerging the probe in the water and held for a couple of minutes to achieve a reliable reading. After the measurement of each sample, the probe was rinsed with de-ionized water to avoid cross-contamination among different samples. All the chemicals used for this study were of analytical grade obtained from BDH (British Drug House, London).

2.3.2 Sample extraction and clean-up

The target analytes were eight PTEs (As, B, Cd, Co, Cr, Ni, Pb, and Se). Water samples were filtrated under vacuum with 0.45 µm and 0.22 µm hydrophilic filters to separate the particulates within 7 days after collection. For heavy metal detection, 5 mL of filtrated water samples were stored in a PVC bottle at 4°C for atomic absorption spectrophotometer analysis.

2.4 Analysis of PTEs

The acidified water samples were used for the analysis of PTEs (B, Cd, Co, Cr, Ni, Pb, and Se) using atomic absorption spectrophotometer (AAS) (PerkinElmer Atomic Absorption Spectrometer pinAAcle 900F) at an analytical wavelength of 405.8, 326.1, and 213.9 nm, respectively. Arsenic content analysis was carried out using Hydride Generation-Atomic Absorption Spectrophotometer (HG-AAS) using Electrode Discharge Lamp at an analytical wavelength of 193.7 nm. For As analysis, 3% $NaBH_4$ (mild reducing agent) and 1.0% NaOH (as a stabilizer for $NaBH_4$) were used, and all the samples were prepared in 1.5% HCl solution.

A standard reference (non-contaminated water sample for B, Cd, Co, Cr, Ni, Pb, and Se and 1.5% HCl for As) was used for quality assurance. The standard solution was made after a series of dilutions of the stock solution (1000 mg/L) considering the limit of detection. The correlation coefficients of calibration curves for each element were found to be>0.99.

2.5 Quality Assurance and Quality Control

A procedural blank and a standard solution consisting of all the reagents were run to check for interferences and cross-contamination for every set of samples. The instrument was calibrated by injection of the standard mixture at seven different concentrations to prepare the standard curve for external calibration purposes. All test batches were evaluated using an internal quality approach and validated if they satisfied the defined internal quality controls. In each batch of experiment run, the blank, certified reference materials (CRM) as an internal standard in samples, and samples were analyzed in duplicate to eliminate any batch-specific error. A multi-element standard solution was used to prepare a standard curve. Before starting the sequence, the relative standard deviation (RSD, <5 %) was checked by using a tuning solution purchased from Agilent company. Five standards with standard linear regression and internal standardization were prepared at levels ranging from 0 to 50 µg/L for As, B, Cd, Co, Cr, Ni, Pb, and Se. The calibration curve was plotted from six points, including the calibration blank.

2.6 Surface Water Contamination Analyses

Four indices namely water quality index (WQI), comprehensive pollution index (P_N), PTE pollution index (PPI) and PTE evaluation index (PEI) were employed to assess the levels of impact of various PTEs concentrations on the overall quality of water in the studied areas. Of these indices, only WQI was calculated by taking into consideration of all physicochemical parameters, whereas the other three indices considered only the PTE concentrations.

2.7 Water Quality Index

Water quality is a very sensitive factor concerning human health and aquatic ecosystems. The Weight arithmetic water quality index (WQI) method is widely used to provide important information on the water matrix by evaluating the comprehensive water quality parameters (physical and chemical parameters) [29,30]. It is considered the most effective method in water quality assessment and water resource management since it provides integrated important information regarding the overall quality for use by regulatory impact analysis [31]. In this study, WQI was calculated using parameters such as pH, EC, TDS, DO, COD, turbidity, total alkalinity, As, B, Cd, Co, Cr, Pb, Ni, Se. The WQI is calculated using equation (1):

$$WQI = \Sigma\ [W_i * (C_i/S_i) * 100] \qquad (1)$$

where $W_i = w_i/\Sigma w_i$ is the relative weighting, w_i is the unit weight of each parameter, and Σw_i is the sum of the weightings of all parameters. Each physicochemical indicator was assigned a specific weight, based on their priority to the relative effect on human health and the significance of different water quality parameters in the overall quality of water for drinking purposes [32]. C_i is the measured concentration of each physicochemical/PTE in the water sample, S_i represents standard permissible limits and the value for each physicochemical/PTE was taken from the Drinking Water Guidelines of WHO [33] and the number 100 refers to the constant. The water quality is classified into five (5) categories based on the numerical values of WQI as follows: excellent: 0–50, good: 50–100, poor: 100–200, very poor: 200–300, and undrinkable: $\geq$300 [32,34].

2.8 Comprehensive Pollution Index

The comprehensive pollution index, P_N, is used for the determination of the contamination status of PTEs in individual water samples. This index is deemed a comprehensive and practical evaluation method [11,35], as shown in the following equations (2) and (3):

$$P_N = \sqrt{}[(P_{i(max))}2 + (P_{i(ave))}2] / 2 \qquad (2)$$

where P_N is the comprehensive pollution index; P_i (= $C_i * S_i^{-1}$) is the single-factor pollution index; C_i is the concentration of the PTEs in water (mg L^{-1}) samples and S_i is the assessment criterion of each PTE (mg L^{-1}). S_i is the maximum allowable concentration (MAC) in water and values obtained from WHO [36] were used. The P_N value of each sample is classified: $P_N \leq 0.7$ as safe, $0.7 < P_N \leq 1.0$ as low contamination, $1.0 < P_N \leq 2.0$ as moderate contamination, $2.0 < P_N \leq 3.0$ as high contamination; and $P_N > 3.0$ as extremely high contamination [11,35].

2.8.1 PTE pollution index (PPI)

The PPI was calculated based on the weighted arithmetic quality mean method. In the present study, eight PTEs (As, B, Cd, Co, Cr, Pb, Ni, and Se) were assessed for the calculation of the PTE pollution index (PPI). PPI is calculated by equation (3):

$$PPI = (\sum[W_i * (C_i\text{-}I_i/S_i\text{-}I_i) *100] * (\sum W_i)^{-1} \qquad (3)$$

Where i stands for different parameters, W_i (= $(Si)^{-1}$) is the unit weight of the ith water quality parameter; C_i is the measured concentration of ith parameter present; I_i is the ideal value of the parameter; S_i is the standard permissible value for the ith water quality parameter and the negative sign (−) denotes numerical difference only. To assess the level of contamination, the PPI values are classified into 3 groups: (i) Low (PPI value < 100); (ii) threshold (PPI value = 100) and (iii) High (PPI value > 100), showing a source of water with no drinking purpose [37].

2.8.2 PTE evaluation index (PEI)

Like PPI, PEI is used to assess the level of pollution caused by PTEs and provides information about overall water quality as regards to PTEs [38,39]. It was evaluated using equation (4):

$$PEI = \sum[PTE_{Conc} * (PTE_{MPC})^{-1}] \quad (4)$$

Where PTE_{Conc} is the monitored concentration of a particular PTE and PTE_{MPC} is the maximum permissible concentration of the same heavy metal. Like WQI, WHO maximum allowable limits for each PTE were used. PEI values are categorized as low pollution (<40), medium pollution (40–80) and high (>80) degree of pollution [39].

2.8.3 PTE toxicity load in water (PTL)

The PTL is an assessment technique which can reliably quantify the level of PTEs in water that may impact human health. This technique can also predict the required removal percentage of the PTEs from the water body to make it safe for human use. It helps document an effective treatment and management plan [40,41]. The PTL is computed by multiplying the measured concentration of PTEs and the hazard intensity score of a given PTE, as shown in equation (5):

$$PTL = \sum C * HIS \quad (5)$$

where C is the observed concentration in this study and HIS is the corresponding hazard intensity score. The HIS is allocated based on the frequency of incidence of toxic metals as a harmful substance by the Toxicological Profiles of the Priority List of Hazardous Substances maintained by the Agency for Toxic Substances and Disease Registry (ATSDR) [42]. The maximum score for a PTE is 1800, where 600 points are allotted for National priorities list (NPL) frequency, toxicity, and potential for human exposure.

2.9 Risk Assessment

Risk assessment is an effective model developed to evaluate the probability of any possible harmful effects on the health of aquatic organisms and humans caused by pollution during a given period, and can be divided into ecological risk assessment and human health risk assessment.

2.10 Ecological Risk

An ecological risk assessment is used to evaluate the potential impact of PTE pollution on organisms in the Niger Delta streams. An ecological risk assessment, according to the different exposure environments of aquatic organisms, can be divided into water risk assessment and sediment risk assessment. In this study, only the surface water risk assessment was conducted and the hazard quotient (HQ) method using was employed to quantify the level of potential ecological risk of PTEs in the surface water bodies. It evaluates the potential damage from PTE contamination by the combined assessment of ecological risk and environmental toxicity. The HQ method is the waterborne concentration divided by the water quality criterion to assess the toxic threat of individual waterborne PTEs. Thus, a hazard quotient calculated using the chronic criteria (HQ_C) provides an assessment of potential chronic toxicity incorporating effects such as impairment of growth and reproductive success. It is expressed by equation (6) [43]:

$$HQ = EC * (ALC)^{-1} \quad (6)$$

where EC_i and ALC_i are the actual exposure concentration of a PTE and corresponding aquatic life criterion values, respectively. The ALC values of 7 PTEs were obtained from Cui et al. [44]. The risk levels were classified as no risk ($HQ < 0.1$), low risk ($0.1 \leq HQ < 1$), moderate risk ($1 \leq HQ < 10$), and high risk ($HQ \geq 10$) [43].

2.11 Human Health Risk Assessment

In aquatic environmental contamination assessment, human health risk measures are calculated to evaluate the potential risk of water contaminants to human health by determining the intensity of contaminant exposure, the level of contaminant exposure, and the dose-response relationship between contaminants and human health. Human beings can be exposed to PTEs in surface water through three pathways, namely direct ingestion, inhalation (through mouth and nose), and dermal absorption. Ingestion and dermal absorption are the main exposure pathways [45,46,47]. Carcinogenic and non-carcinogenic risk assessment was conducted to estimate health effects on the inhabitants of the study area due to exposure to PTEs.

The carcinogenic effect of PTEs is computed throughout a lifetime, taking into consideration exposures during both childhood and adulthood [48,49]; a child aged 0-15 years and an adult aged 15-54.7 years [50]. The lifetime exposures due to incidental ingestion and dermal absorption of water (carcinogenic effect) for a receptor (child or adult) were computed according to equations (7) and (8):

$$CE_{ing} = \frac{IR * EF * ED}{BW * AT} \qquad (7)$$

$$CE_{der} = \frac{Kp * tevent * ET * SA * EF * ED}{BW * AT} \qquad (8)$$

where CE_{ing} and CE_{der} (L kg^{-1} day^{-1}) refers to exposure due to ingestion and dermal contact, respectively of water (carcinogenic effect), IR (L day^{-1}) is the daily water ingestion rate for a receptor (child or adult), EF (day yr^{-1}) is the exposure frequency for a receptor, ED (yr) is the exposure duration for a receptor, BW (kg) is the average body weight of a receptor, AT (day) is the average time for carcinogenic effect, ET is the exposure time of swimming (hours/day), SA is the skin surface area exposed (cm^2) and K_p is the skin permeability constant (cm hr^{-1}).

The estimated values of input parameters for assessing exposure via ingestion and dermal absorption in equations (7), (8) and (9) are presented in Table 1.

Potential lifetime carcinogenic health effects (LCR) to the local population resulting from incidental ingestion of water and dermal absorption were calculated according to Equation (9). The cancer risk was assessed for carcinogenic As, Cd, Cr, Ni and Pb (classified as human carcinogens and possible human carcinogens by IARC [51] which have oral cancer slope factors (SF_o) reported.

$$CR_{ing/der} = CE_{ing/der} * C_w * ABS_{gi/d} * SF_{o/der} \qquad (9)$$

$$CR_{Adult} = \sum(CR_{ing} + CR_{der})_{i,\ Adult} \qquad (10)$$

$$CR_{Child} = \sum(CR_{ing} + CR_{der})_{i,\ Child} \qquad (11)$$

Table 1. Parameters and input assumptions for exposure assessment of PTEs through ingestion and dermal pathways

Parameter	Units	Values		Reference
		Adult	Child	
Concentration of PTE in water, C_w	µg L^{-1}	this study	this study	
Incidental ingestion rate/event, IR	L day^{-1}	0.053	0.098	[58]
Event frequency, EV	day	1	1	Assumption
Daily event duration, ET	h day^{-1}	0.58	1	[52]
Exposure frequency for recreation, EF	days y^{-1}	350	350	[52]
Exposure frequency, ED	years	24	6	[52]
Exposed skin surface area, SA (cm^2)	cm^2	18,100	6600	[52]
Gastrointestinal absorption factor, ABS_{gi}	-	As, B, Co: 1, Cd: 0.05, Cr: 0.038, N: 0.2, Pb: 0.117, Se: 0.85		[52]
Dermal Absorption factor, ABS_d	-	As: 0.03; others: 0.001		[52]
Dermal permeability coefficient, K_p	cm h^{-1}	As, B, Cd, Se: 0.001, Co: 0.0004, Cr:0.002, Ni: 0.0002, Pb: 0.0001		[52]
Body weight, Bw	Kg	70	15	[52]
Lifetime, LT (y)	years	54.7		[50]
Average time, AT	days	365 x LT		[52]
Oral Slope Factor , Sf_o	kg d mg^{-1}	As: 1.5, Cd: 0.38, Cr: 0.5, Ni: 1.7, Pb: 0.0085		[52]

The cancer slope factor to dermal absorption (SF_{der}) is derived according to USEPA [52] by dividing the SF_o with ABS_{gi}.

The summation of the risk due to the different exposure pathways for both age groups provides the aggregate lifetime carcinogenic risk for each contaminant risk, calculated by equation (12):.

$$LCR = CR_{Adult} + CR_{Child} \quad (12)$$

The range of acceptable or tolerable risk value is 10^{-6} to 10^{-4} and unacceptable if the risks are surpassing 1×10^{-4} while the risks below 1×10^{-6} are not likely to pose significant health hazards [53,54].

2.12 Statistical Analysis

The pollution status of PTEs, ecosystem risk assessment of PTEs, and human health risk assessment of PTEs were analysed by using Microsoft Excel 2007 software. The analysis of source characteristics of PTEs was based on the use of Excel 2020 and SPSS 20.0 software.

3. RESULTS AND DISCUSSION

The results presented in this study comprise an attempt to report the levels, water quality index based on physicochemical and PTE parameters, and contamination status using a comprehensive pollution index, PTE pollution index, PTE evaluation index, toxicity load and percentage removal of PTE load to make the water suitable for human consumption, associated ecological risk to aquatic organisms and human health risk to inhabitants due to using the streams for recreation in Niger Delta, Nigeria.

3.1 Water Quality Parameters

The physicochemical parameters such as temperature, pH, EC, TDS, DO, BOD, COD, turbidity and alkalinity of water of Niger Delta streams are shown in Table 2. Water temperature ranged from 29-30.8ºC with an average of 29.7ºC and above the WHO[33] guidelines of 25ºC. High-temperature stress aquatic ecosystem by reducing the ability of water to hold essential dissolved oxygen and directly the water organisms. The pH ranged from 5.91-6.73, with an average value of 6.4 which was within the WHO's permissible limit (6.5-8.5) for portable water. The electrical conductivity (EC) values ranged between 854.7 and 1618 µS cm^{-1} with an average value of 1207.8 µS cm^{-1}. The high level of EC (>WHO's limit of 750 µS cm^{-1} and USEPA's 1000 µS cm^{-1}) was due to the significant amount of dissolved salt in the water under study. Total dissolved solids (TDS) comprise inorganic salts and small amounts of organic matter that are dissolved in water. The TDS values at the various sampling sites ranged from 511.6- 967.9 mg L^{-1}, with an average of 723 mg L^{-1} higher that the WHO and USEPA limits of 500 mg L^{-1}. The electrical conductivity of water is a direct function of its total dissolved solids. According to Chapman [55] and Addo et al. [56], TDS may be obtained by multiplying the conductivity by a factor between the range of 0.55-0.75 and in this study statistics, the TDS is directly a multiplication factor of 0.6 of the conductivity values measured across the three streams investigated. Dissolved oxygen (DO) gives a ready assessment of the purity of water and is very essential for the survival of aquatic organisms. The measured DO values varied from 4.90 to 7.53 mg L^{-1} with an average of 5.8 mg L^{-1}. The measured values and average are lower than the WHO [33] regulatory limit of 10 mg L^{-1}. Low DO values might be due to higher microbial activities for instance decomposition of organic matter might be an important factor in the consumption of DO. Very low DO may affect the survival of aquatic organisms and may result in anaerobic conditions that can cause bad odour in water.

The BOD and COD are important indicators of the amount of organic load or pollution in the water body that is they are used to measure the health of the stream water. The BOD and COD measurements were 19.1-59.4 and 130.7-317.6 mg L^{-1} respectively. The recommended BOD and COD values for drinking water are 6 and 10 mg L^{-1}, respectively [33]. The high BOD and COD values indicated that the stream was severely polluted and these high values of the sections' water may be accounted for by untreated effluents from the oil and gas facilities as well as effluents from domestic sewage. Turbidity is a measure of the cloudiness of a water body. It is used to indicate water quality and filtration effectiveness (e.g., whether disease-causing organisms are present). The measured values in this study ranged from 0.19-0.97 NTU which is lower than the WHO [33] permissible limit of 5 NTU. This range falls within the 0.1- 4.0 NTU reported by Abowei et al. [57].

Table 2. Statistical summary of the overall mean of measured parameters of surface water samples of Niger Delta streams

	Overall mean	Range	Permissible limits	
			33	53
Physicochemical				
Temperature	29.71	29-30.8	25	25
Hydrogen ion concentration (pH)	6.38	5.91-6.73	6.5-8.5	6.5-8.5
Electrical Conductivity (EC)	1207.80	854.7-1618	750.00	1000.00
Total Dissolved Solids (TDS)	723.08	511.6-967.9	500	500
Dissolved Oxygen (DO)	5.82	4.9-7.53	10	6a
Chemical Oxygen Demand (COD)	246.96	130.7-317.6	10	200
Biological Oxygen Demand (BOD)	34.7	19.1-59.4	6	<6.0
Turbidity	0.67	0.19-0.97	5	10
Total Alkalinity (TA)	279.98	232-315.6	200	200
Concentration of PTEs				
Arsenic (As)	610	380-760	10	10
Boron (B)	60	30-90	2400	1000
Cadmium (Cd)	593.33	320-880	3	5
Cobalt (Co)	1080	320-1680	40	10
Chromium (Cr)	1853.33	1340-2330	50	100
Lead (Pb)	2520	1490-3580	10	15
Nickel (Ni)	2623.33	780-5510	70	100
Selenium (Se)	746.67	30-1350	40	50
PTE load	10086.67	807-1155		

All units are in µg L^{-1} except temperature (◦C), pH, EC (µS/cm) and turbidity (NTU)

3.2 Distribution of PTEs in Water

A statistical summary of PTEs' overall mean concentration (mg L^{-1}) and ranges in the surface water of the tidal streams is given in Table 2 while the mean concentration of PTEs in water from the sampled communities is shown in Fig. 2. The concentration of PTEs in Buguma stream decrease in the order Pb > Cr > Ni > Cd > As > Co > B > Se. Pb (30.86%), Co (28.87%) and Ni (19.58%) contributed 79.31% of the total PTE load. In the surface water of Krakrama stream, PTEs concentration decrease in the order Pb > Cr > Co > Se > Ni > As > Cd > B while those in Bonny stream followed the trend Ni > Pb > Cr > Co > Se > As > Cd > B. Pb and Ni contributed 33.65% and 47.69% of the total PTE load in Krakrama and Bonny streams, respectively. The mean concentrations in the sampled tidal streams of the Niger Delta were above the permissible limits of WHO[33] and USEPA[53] except B (Table 2), indicating heavy contamination of the streams. Consequently, potential carcinogenic health risk assessment of the PTEs in surface water from the streams was justified.

3.3 Contamination Status

Contamination-level classification for water quality index (WQI), comprehensive pollution index (P_N), PTE pollution index (PPI) and PTE evaluation index (PEI) of studied water samples are presented in Table 3. The WQI is one of the best tools for monitoring surface water contamination and can be used for water quality improvement programs. In this study, the water quality assessment at the three tidal streams is evaluated using the WQI method. The pH, EC, TDS, DO, COD, turbidity, alkalinity, As, B, Cd, Co, Cr, Pb, Ni and Se were taken into account for the calculation of the WQI value for each water body. The World Health Organization [58] limits were utilized for calculations. The computed WQI values ranged from 2311 to 2924, with an average of 2668.7. The surface water in the three water bodies was deemed undrinkable with WQI values $\geq$300. The water quality of the tidal streams is unsuitable for consumption and other domestic purposes mainly due to input of oil spills, used two-stroke engine lubricating oil, urban and industrial wastes and/or agricultural activities discharged into the streams.

WQI evaluation of surface water samples from the tidal streams demonstrate that there is a high level of contamination, hence requires treatment before use. The main contributors to the WQI are Cd (45.4%), Cr (14.2%), Ni (10.0%) and Pb (9.6%). According to the computed PEI values, water samples from the three tidal streams were classified as heavily contaminated (>80) while P_N values classified them as extremely high. The estimated PPI values classified the water samples from three streams as unsuitable for drinking.

3.4 PTE Toxicity Load

Toxicity load (TL) is used to evaluate the pollution load of PTEs in water bodies and give the quantity (in percentage) of PTEs to be removed to make the water suitable for human use [59]. The PTE toxicity load determines the content of PTEs in surface water bodies that results in non-carcinogenic risk as well as assists in providing an efficient treatment and management plan [41,60]. The PTE toxicity load was computed for As, B, Co, Cd, Cr, Ni, Pb and Se using the hazard intensity scores obtained from the ATSDR substance priority list [42]. The PTL values ranged from 9,631 to 12,658 mg L^{-1} with an average PTL of 11, 626 mg L^{-1} (Table 4). The calculated PTL values of the three streams were higher than the permissible toxicity load, 1,276 mg L^{-1} (Table 4). The pollution load due to the PTEs except B were above the permissible toxicity loads (As: 16.8, Cd: 4.0, Co: 40.6, Cr: 44.6, Pb: 15.3, Ni: 69.6 and Se: 31.2 mg L^{-1}). Therefore, the removal of these heavy metals is essential from the surface water bodies to safeguard human health. Details of the required removal percentage of the PTEs from the surface water of each stream to mitigate the health hazard are shown in Table 4. Maximum of 99%, 100%, 98%, 98%, 100%, 99%, and 97% removal of As, Cd, Co, Cr, Pb, Ni, and Se is essential to make the water suitable to use for human activities.

3.5 Risk Assessment

3.5.1 Ecological risk assessment

The ecological risk of the studied PTEs in the surface water samples from the three streams is shown in Fig. 3. The results showed that the computed HQ values of As, B, Co, Cr, Pb, Ni and Se in water samples were below 10 indicating moderate risk to aquatic organisms. The trend of ecological risk of the PTEs in Buguma, Krakrama and Bonny streams were as: Se > Cd > Co > Ni > Pb > Cr, Co > Cd > Ni > Cr > Pb > Se and Co > Pb > Cd > Ni > Cr > Se, respectively. The contribution of the more dominant PTEs to the ecological risk in each water body was Se (45.40%) and Cd (27.13%) in Buguma, Co (62.47%) and Cd (18.56%) in Krakrama and Co (55.43%) and Pb (20.43%) in Bonny. The overall risk of the streams was classified as moderate.

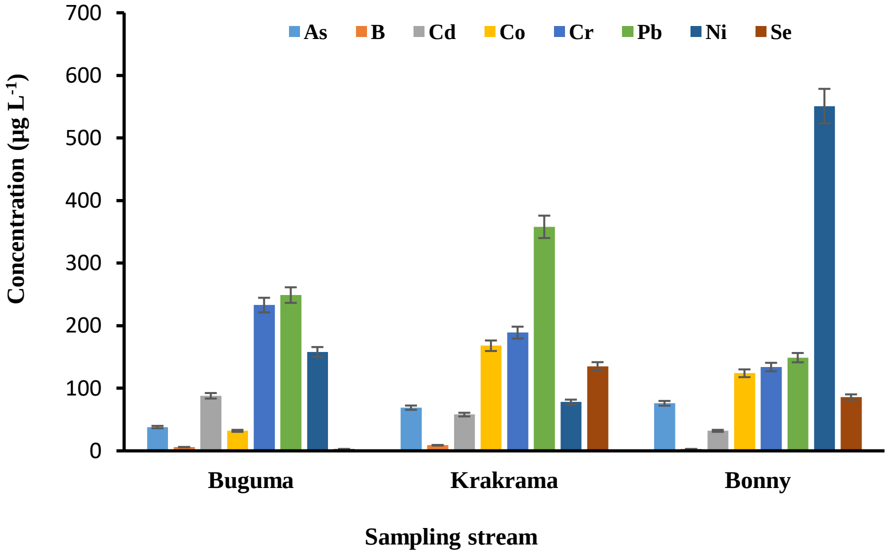

Fig. 2. Concentration of PTEs in the water of Niger Delta streams

Table 3. Pollution-level classifications for water quality index (WQI) [32], comprehensive pollution index (P_N) [35], and PTE pollution index (PPI) [37], and PTE evaluation index (PEI) [39]

WQI			P_N			PPI			PEI		
Value	**Water quality**	**Sample ID**	**Value**	**Pollution level**	**Sample ID**	**Value**	**Characteristic**	**Sample ID**	**Value**	**Pollution level**	**Sample ID**
< 50	Excellent	-	< 0.7	Safe	-	< 100	Suitable for drinking		< 40	Low	-
50–100	Good water	-	0.7 - <1.0	Low	-	> 100	Unsuitable for drinking	L1, L2, L3	40–80	Medium	-
100–200	Poor water	-	1.0 - < 2.0	Moderate	-				> 80	High	L1, L2, L3
200–300	Very poor water	-	2.0 - < 3.0	High	-						
> 300	Unsuitable for drinking	L1, L2, L3	> 3	Extremely high	L1, L2. L3						

Note: L1 = Buguma stream, L2 = Krakrama stream and L3 = Bonny stream

Table 4. Toxicity load (PTL, mg L^{-1}) of the surface water based on the relative level of PTEs and required percentage removal of PTE for safety

Sampling creek	**As**	**B**	**Cd**	**Co**	**Cr**	**Pb**	**Ni**	**Se**	**PTL**
Buguma	637	26	1,159	325	2,078	3,812	1,571	23	9,631
Krakrama	1,156	40	764	1,705	1,686	5,481	775	1,052	12,658
Bonny	1,273	13	421	1,259	1,195	2,281	5,477	670	12,590
Average	1,022	26	781	1,096	1,653	3,858	2,608	582	11,626
[a]Hazard intensity score (HIS)	1,675	439	1,317	1,015	892	1,531	994	779	
Permissible toxicity load (mg L^{-1})	16.8	1,054	4.0	40.6	44.6	15.3	69.6	31.2	1,276
Removal of PTE to reduce pollution load									
Buguma	97%	OK	100%	Ok	98%	100%	96%	OK	
Krakrama	99%	OK	99%	98%	97%	100%	91%	97%	
Bonny	99%	OK	99%	97%	96%	99%	99%	95%	

[a]ATSDR[42], OK: within permissible toxicity load

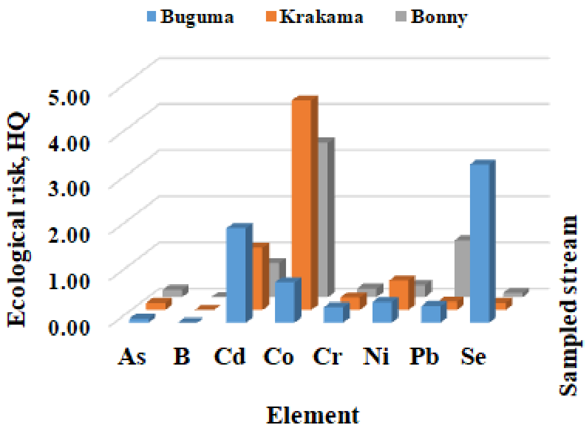

Fig. 3. Ecological risk assessment (HQ) of PTEs in surface water of Niger Delta streams

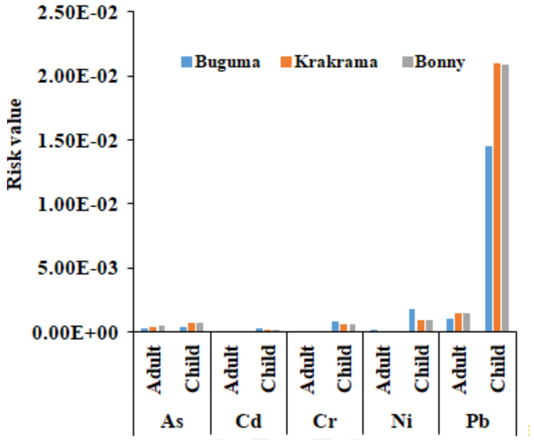

Fig. 4. The cancer risk of individual PTEs in surface water samples from Niger Delta streams

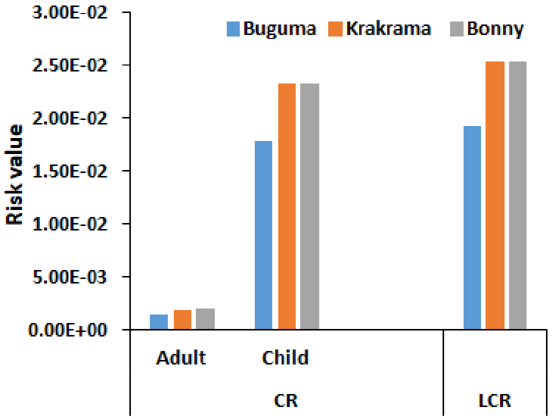

Fig. 5. Cancer risk and lifetime cancer risk of PTEs in surface water samples from the tidal streams

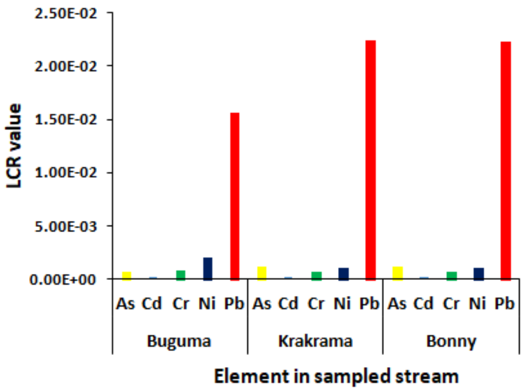

Fig. 6. Lifetime cancer risk of individual PTEs in surface water samples from Buguma, Krakrama and Bonny streams

3.6 Health Risk Assessment

3.6.1 Lifetime cancer risk (LCR)

The distribution of the carcinogenic risk of children and adults, and lifetime cancer risk of PTEs exposure via two pathways in the study area was shown in Figs. 4, 5 and 6. According to Maertens et al. [61] cancer risk values above 1×10^{-4} (one cancer case per ten thousand people) are not acceptable. The cancer risk of the PTEs for both children and adults, except Cd and Cr for adult, ranged from 1.52×10^{-4} to 2.09×10^{-2} and 1.06×10^{-4} to 1.43×10^{-3}, respectively. This means that there was cancer risk associated with As, Pb and Ni due to incidental ingestion and dermal contact with surface waters of three streams sampled. Long-term recreation activities at the streams and the incidental ingestion of water will result to As-, Pb- and Ni-associated cancer risk for children and adults, Cd- and Cr-initiated cancer risk for children. The lifetime risk values of in the sampled stream waters ranged from 1.56×10^{-4} to 2.24×10^{-2} (Fig. 6). Among the PTEs, Pb was the most influencing and contributed 80.64%, 88.30% and 88.14% to the lifetime cancer risks resulting ingestion and dermal absorption of the surface waters from Buguma, Krakrama and Bonny streams, respectively. The LCR values of the PTEs and in the streams followed the decrease order: Pb > Ni > As > Cr > Cd and Bonny = Krakama >Buguma, respectively. The study is helpful to avoid the possibility of increasing contamination of surface water and in ensuring public safety.

4. CONCLUSION

In this study, levels of PTEs present in the surface water of three streams of the Niger Delta were measured and associated ecological and human health risks were estimated. Also, the water quality index, the toxicity load and the necessary percentage removal of PTEs to make the water safe for human consumption were evaluated. The PTE concentrations in all the samples from the studied streams were above the recommended limits of FAO/WHO. Due to similar pollution sources, other pollutants like PAHs and PCBs have often been found to co-exist with PTEs, therefore, the risk computed is likely underestimated because of the non-inclusion of other contaminants. The average values of CR of surface waters samples from the three streams were above the recommended threshold of 1×10^{-4} for PTEs. High levels and ecological and human health risks of PTEs in riverine communities of Buguma, Krakrama and Bonny could be a result of indiscriminate discharges of untreated industrial effluents, domestic wastage and illegal bunkering occurring at the streams. The examined water bodies in the Niger Delta were found to be unsafe for human consumption and hence have the potential to cause an adverse health effect for both children and adult populations. Therefore, ecological and human health risk assessment showed that surface water from the three streams in the Niger Delta was more polluted. Because of this, it is recommended that stakeholders and policymakers should help in crafting policies and strategies to mitigate the level of crude oil pollution, and consequently in reducing PTEs contamination of drinking water as well as to monitor PTEs pollution in surface waters of the coastal communities of Buguma, Krakrama and Bonny for sustainable ecosystem and human health.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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