

# Public Health Risk Assessment of Treated and Untreated Produce Water Effluent

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## ARTICLE INFO

### Article History:

Accepted: 05 June 2023

Published: 19 June 2023

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### Publication Issue

Volume 10, Issue 3

May-June-2023

### Page Number

941-955

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## ABSTRACT

Discharge of produced water into the aquatic environment may release chemicals that are highly toxic to sensitive marine species even at low concentrations, causing bio-degeneration/transformation of the biota. Some metals and hydrocarbons may accumulate in sediments, bio-accumulate in bottom living biological communities which may pose threat to humans and animals. Physicochemical quality of untreated and treated produced water were assessed. Toxicity and pollution levels as well as human health risk assessment of treated and untreated produced water were also determined to ascertain the level of environmental safety vis-à-vis effects of treatment, in order to identify potential environmental concerns from existing treatment practices. Microbial density and concentration of eight heavy metals in produced water samples were assessed following standard procedures and different indices were used to assess the health risk. Concentration (in mg/L) of iron was 6.9 (untreated) and 0.001 (treated wastewater), arsenic 0.001 for both untreated and treated wastewater, zinc (0.002 for both untreated and treated wastewater), mercury (0.001 for both untreated and treated wastewater), chromium (0.001 for both untreated and treated wastewater), cadmium (1.1 for untreated and 0.001 for treated wastewater), lead (0.9 for untreated and 0.001 for treated wastewater) and nickel (0.005 for both untreated and treated wastewater). Further, statistical analysis showed correlation between physicochemical parameters of untreated and treated wastewater as well as heavy metal concentrations. Health risk assessment showed major potential non-carcinogenic risk was via ingestion, with lead as the main contributor. Overall non-carcinogenic risk evaluation of produced water showed that humans are not susceptible. Similarly, chromium was the major contributor to the carcinogenic health risk but values for lethal average daily doses and cumulative carcinogenic risk were within permissible limits.

Keywords: Produced Water, Heavy Metals, Health Risk Assessment

## I. INTRODUCTION

Toxins may inadvertently be introduced as chemical additives to improve drilling and production operations or they may leach into the produced water from the formation rock or the drilled hydrocarbon. Other compounds in the produced water include total organic carbon, organic acids, heavy metals, radioisotopes etc. Produced water often is generated during the production of oil and gas from onshore and offshore wells. Formation water is seawater or fresh water that has been trapped for millions of years with oil and natural gas in a geologic reservoir consisting of a porous sedimentary rock formation between layers of impermeable rock within the earth's crust (Sheikholeslami *et al.*, 2018).

When a hydrocarbon reservoir is penetrated by a well, the produced fluids may contain this formation water, in addition to the oil, natural gas, and/or gas liquids. Fresh water, brine/seawater, and production chemicals sometimes are injected into a reservoir to enhance both recovery rates and the safety of operations. These surface waters and chemicals sometimes penetrate to the production zone and are recovered with oil and gas during production (Saleh and Gupta, 2014; Nasiri *et al.*, 2017).

Produced water (formation and injected water containing production chemicals) represents the largest volume of waste stream in oil and gas production operations on most offshore platforms. Produced water may account for 80% of the wastes and residuals produced from natural gas production operations (Ajuzeiogu *et al.*, 2018; Jimenez *et al.*, 2018). The inorganic content of produced water is highly related to the geochemical characteristics of the well. They present as dissolved salts, naturally occurring radioactive materials and heavy metal.

Cations such as Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup>, Fe<sup>2+</sup> and anions such as Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> affect produced water chemistry in terms of buffering capacity, salinity, and scale potential (Hildenbrand *et al.*, 2018), salinity, mainly due to dissolved sodium and chloride and in a lower extent to calcium, magnesium and potassium, may vary from a few parts per million to about 300000 mg/L (Pitre, 2013; Estrada and Bhamidimarri, 2016, USEPA, 2022).

Lesser volumes of heavy metals such as cadmium, chromium, copper, lead, mercury, nickel, silver and zinc mostly occur naturally (Chikwe and Okwa, 2016). Lead is a toxic metal that enters a body through ingestion, inhalation, and skin absorption and can be accumulated in tissue. This affects most organs in human body especially the kidneys and brain (Tarrago and Brown, 2012; Bodrud-Doza *et al.*, 2019). Chromium is also toxic and water contaminated with chromium, results to skin irritation, livestock death, etc. Their concentration can reach 10<sup>2</sup> to 10<sup>5</sup> times the one found in seawater. Naturally occurring radioactive materials (NORM) originated from the geological formation and are brought to the surface as dissolved solids in produced water. NORM may precipitate into scale or sludge when water temperature reduces as it reaches the surface. The most abundant NORM compound is <sup>226</sup>Ra and <sup>228</sup>Ra and barium and this is derived from the radioactive decay of uranium-238 and thorium-232 associated with certain rocks and clay in the hydrocarbon reservoir (Lee and Neff, 2011; Al-Ghouti *et al.*, 2019). When radium decays, it emits alpha and gamma rays, and exposure to radium causes cancer.

Physicochemical parameters of treated and untreated produced water effluent were conducted, and the concentration of eight (8) heavy metals namely iron,

arsenic, zinc, mercury, chromium, cadmium, lead and nickel was determined in wastewater samples following standard procedures. Toxicity and pollution levels as well as human health risk assessment of treated and untreated Produced water effluent were also determined to ascertain the level of environmental safety vis-à-vis effects of treatment, in order to identify potential environmental concerns from existing treatment practices.

## II. MATERIAL AND METHODS

### 2.1 Sample collection

Samples of produced water (untreated and treated) were collected from an offshore operational facility situated in Akwa Ibom State with GPS coordinate 03°51.141N; 006°58.794'E.

A 10 -liter sampling container was used for sample collection prior to the initiation of testing with test organisms. Sample for BOD was collected in amber bottles. Sterile plastic bottles were used to sample for

microbial analysis of the test sample. All samples were stored at 4°C prior to testing. One (1) litre glass bottles were used to sample for total petroleum hydrocarbon and was preserved with 1:1 sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), while sample for heavy metals was preserved by 1:1 Nitric acid (HNO<sub>3</sub>).

### 2.2 Physicochemical analysis

Produced water samples were analysed following standard procedures according to American Public Health Association (APHA, 2018).

### 2.3 Statistical analysis

Multivariate analyses, including Pearson’s correlation analysis were effective tools to identify the sources of heavy metals. Pearson’s correlation analysis was used to evaluate the relativity between physicochemical parameters as well as heavy metal elements (Shen and Schaffer, 2018).

### 2.4 Pollution evaluation indices

Pollution level of treated and untreated wastewater was determined using heavy metal evaluation index (HEI), contamination factor (C<sub>f</sub>), and degree of contamination (C<sub>deg</sub>). These indices were determined to investigate the drinking suitability of effluent water on water bodies (Table 1). The HEI gives an insight on the overall quality of wastewater for trace metals (Bodrud-Doza *et al.*, 2019), and calculated as follows:

$$HEI = \sum_{i=1}^n \left( \frac{H_c}{H_{mac}} \right) \dots\dots\dots \text{Equation 1}$$

Where H<sub>c</sub>= monitored value; and H<sub>mac</sub>=maximum admissible concentration (MAC) of the i<sup>th</sup> parameter. The degree of heavy metal index was classified into three divisions; HEI≤10: low; HEI (10-20): medium; and HEI>20: high (Bodrud-Doza *et al.*, 2019).

**Table 1: Pollution evaluation index classification**

Contamination Factor (C <sub>f</sub> )	Extent of Contamination	C <sub>deg</sub>	Extent of Contamination	HEI	Extent of Contamination
C <sub>f</sub> < 1	Low	C <sub>deg</sub> < 1	Low	HEI ≤ 10	Low
1 < C <sub>f</sub> ≤ 3	Moderate	C <sub>deg</sub> (1-3)	Medium	HEI (10-20)	Medium
3 < C <sub>f</sub> ≤ 6	Considerable	C <sub>deg</sub> > 3	High	HEI > 20	High
C <sub>f</sub> > 6	Very High				

The  $C_f$  was used for accessing the degree of metal contamination of wastewater. The  $C_{deg}$  indicates the overall effects of each contaminant or water quality parameters (Islam *et al.*, 2016), and calculated by the following equation:

$$C_{deg} = \sum_{i=1}^n (C_{fi}) \dots \dots \dots \text{Equation 2}$$

Where  $C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1$ ;  $C_{fi}$  = Contamination Factor;  $C_{Ai}$ = analytical value of the  $i^{th}$  component;  $C_{Ni}$ = Upper permissible concentration of the  $i^{th}$  component ( $C_{Ni}$ =MAC), and  $N$ = normative value.

## 2.5. Human Health Risk Assessment

Human health risk assessment was employed to evaluate possible risk of exposure of treated wastewater to humans (children and adults). Chronic risk assessment and carcinogenic risk assessment were determined to evaluate long term effect of exposure.

### 2.5.1 Chronic Risk Assessment

The health risk assessment of each heavy metal is usually based on quantification of the risk level and is expressed in terms of carcinogenic and non-carcinogenic health risk (USEPA 2014). According to the USEPA (2015) the two principal toxicity risk factors evaluated were the Slope Factor ( $SF$ ) for carcinogen risk characterization, and the reference dose ( $RfD$ ) for non-carcinogenic risk characterization (Table 2). The trio of ingestion, inhalation and dermal exposure pathway for daily dose intake by adult and children were considered for the assessment (Table 3).

The dose intake by dermal contact [ $D_{derm}$ (mg/kg/day)] is expressed as:

$$D_{derm} = \frac{C \times S \times A \times S_L \times A_{BS} \times E \times F \times E \times D}{B \times W \times A \times T} \times 10^{-6} \dots \dots \dots \text{Equation 3}$$

The dose intake by inhalation of contaminants [ $D_{inh}$ (mg/kg/day)] is expressed by:

$$D_{inh} = C \text{ (mgperkg)} \times \frac{I \times n \times R \times E \times F \times E \times D}{P \times E \times F \times B \times W \times A \times T} \dots \dots \dots \text{Equation 4}$$

The dose intake by ingestion [ $D_{ing}$ (mg/kg)] is expressed as:

$$D_{ing} = \frac{C \times I \times n \times R \times E \times F \times E \times D}{B \times W \times A \times T} \times 10^{-6} \dots \dots \dots \text{Equation 5}$$

Where  $SA$ =Exposed surface area ( $cm^2/day$ );  $SL$ =Skin adherence factor ( $mg/cm^2/day$ );  $ABS$ = skin Absorption Factor,  $EF$ = Exposure frequency (days/year);  $ED$ = Exposure Duration (years);  $BW$ = Body weight (kg);  $AT$ = Averaging Time (days);  $PEF$ = Particulate Emission Factor;  $C$ = concentration (mg/l) of a given element in the wastewater; and  $IngR$ = ingestion rate (mg/day).

**Table 2 :** Reference Doses (RfD) for non-carcinogens and Slope Factors (SF)

Element	RfD mg/kg/day			SF/Kgdmg <sup>-1</sup>
	RfD <sub>ing</sub>	RfD <sub>Derm</sub>	RfD <sub>inh</sub>	
Chromium, Cr	3.00E-03	6.00E-05	2.86E-05	4.20E+01
Arsenic	3.00E-04			1.50E+00
Zinc	3.00E-01	-	-	-
Iron	7.00E-01	-	-	-
Mercury	1.60E-04			-
Lead, Pb	1.40E-03	5.25E-05	3.52E-03	8.50E-03 (ing) 4.20E-02 (Inh)
Nickel, Ni	2.00E-02	5.40E-03	2.06E-02	8.40E-01
Cadmium, Cd	1.00E-03	1.00E-05	1.00E-05	6.30E+0

To further define the non-carcinogenic risk if exposed, the following equation is used:

$$HQ = \frac{DI}{RfD} \dots \dots \dots \text{Equation 6}$$

Where HQ = Hazard Quotient for a given exposure route, DI= Dose intake via a given exposure route, RfD= Reference Dose for a particular element through a particular exposure route. If HQ>1, there is an unacceptable risk of adverse non-carcinogenic effects on health. While if HQ<1, it is an acceptable level (USEPA, 2001; Giri and Singh, 2015). RfD for no-carcinogens and SF for carcinogens are as listed in Table 2. Table 3 presents the guidance values for the determination of dose intake (Bankole, 2018). To determine the overall risk through the two pathways (ingestion and dermal), the Hazard Index (HI) expressed by Equation 7 was used.

$$HI = HQ(ing) + HQ(inh) + HQ(derm) \dots \dots \dots \text{Equation 7}$$

Where HI = Hazard Index, HQ (HQ<sub>ing</sub>, HQ<sub>inh</sub> and HQ<sub>derm</sub>) represents the Hazard Quotients for ingestion, inhalation and dermal pathways for exposure respectively.

If HQ<1, no chronic risk is assumed to occur at the site. If HI>1, it implies that there is non-carcinogenic health risk (Yang *et al.*, 2012).

**Table 3 :** Guidance Values for the Determination of Dose Intake

Symbol	Definition	Child	Adult
IngR	Ingestion Rate (mg/day)	200	100

<b>EF</b>	Exposure Frequency (days/year)	350	350
<b>ED</b>	Exposure Duration (years)	6	24
<b>BW</b>	Body Weight	15	61.8
<b>AT</b>	Averaging Time (days)	ED X 365 = 2,190	ED X 365 = 8,760 (for carcinogenic risk, 72 X 365 = 26,280)
<b>InhR</b>	Inhalation Rate (m <sup>3</sup> /day)	7.63	12.8
<b>PEF</b>	Particulate Emission Factor (m <sup>3</sup> /kg)	1.316E+09	1.316E+09
<b>ABS</b>	Skin Absorption Factor	0.001	0.001
<b>SA</b>	Exposed Surface Area (cm <sup>2</sup> /day)	2800	5700
<b>SL</b>	Skin Adherence Factor (mg/cm <sup>2</sup> /day)	0.2	0.07

### 2.5.2. Carcinogenic Risk Assessment

For carcinogens, the lifetime average daily dose (LADD) for inhalation exposure was used in the assessment of the cancer risk (Bankole, 2018). The LADD is expressed as:

$$LADD = \frac{C \times EF}{PEF \times AT} \times \left( \frac{InhR(\text{child}) \times ED(\text{Child})}{BW(\text{child})} \times \frac{InhR(\text{Adult}) \times ED(\text{Adult})}{BW(\text{Adult})} \right) \dots \text{Equation 8}$$

The potential cancer health risk was obtained by the product of the lifetime average daily dose and the inhalation slope factors for each of the heavy metals.

$$R_{(\text{total})} = \sum_{i=1}^m \sum_{j=1}^n (LADD \times S.F)_{ij} \dots \text{Equation 9}$$

Where: R<sub>(total)</sub> = cumulative carcinogenic risk or total cancer risk for carcinogenic metals.

R<sub>(total)</sub> > 1E-04, not acceptable; R<sub>(total)</sub> = 1E-06, pose no significant health risk; R<sub>(total)</sub> between 1E-04 to 1E-06, are generally considered acceptable on the situation and circumstances of exposure.

## III.RESULTS AND DISCUSSION

### 3.1 Heavy metals concentration of treated and untreated wastewater

The results of heavy metals in untreated and treated wastewater are presented in Table 4. Concentration of individual heavy metals with respect to tolerable limits are presented in Figure 1.

The concentration of lead (Pb) in wastewater of study reduced considerably from 0.9mg/L to below 0.001mg/L. Though the USEPA and the CDC agrees that there is no known safe level of Pb in a child's blood or in drinking water, WHO (2011) considers 0.05mg/L as the maximum tolerable limits for wastewater effluents. In either case, the value of untreated wastewater according to the study falls above WHO permissible limits. However, treatment of the wastewater greatly reduced this value to below detectible limits. According to USEPA (2022), young children, infants, and fetuses are particularly vulnerable to lead because the physical and behavioral effects of lead occur at lower exposure levels in children than in adults. A dose of lead that would have little effect on an adult can have a significant effect on a child. In children, low levels of exposure have been linked to damage to the central and peripheral nervous system, learning disabilities, shorter stature, impaired hearing, and impaired formation and function of blood cells (USEPA, 2022). The range of chromium (Cr) concentration in wastewater were found to be below 0.001mg/L. These values fall within permissible limits of 0.03mg/L (WHO, 2015). The concentration of iron (Fe) present in sampled wastewater reduced from 6.9±0.0mg/L to 0.001mg/L.

**Table 4 :** Results of heavy metal concentration of treated and untreated waste water

Parameter	Waste	Water	Waste water	Maximum Permissible Limit	
	(Untreated)		(Treated)	Limit	Source
Iron, mg/L	6.9±0.00		0.001±0.00	1.0	EGASPIN, 2018
Arsenic, mg/L	0.001±0.00		0.001±0.00	0.1	WHO, 2022
Zinc, mg/L	0.002±0.00		0.002±0.00	1.0	EGASPIN, 2018
Mercury, mg/L	0.001±0.00		0.001±0.00	0.1	WHO, 2022
Chromium, mg/L	0.001±0.00		0.001±0.00	0.05	EGASPIN, 2018
Cadmium, mg/L	1.1±0.00		0.001±0.00	1	WHO, 2022
Lead, mg/L	0.9±0.00		0.001±0.00	0.05	EGASPIN, 2018
Nickel, mg/L	0.005±0.00		0.005±0.00	0.07	EGASPIN, 2018

Iron concentration of treated wastewater was found to be within World Health Organization standards of 1mg/L. Being a crucial component of the hemoglobin, an oxygen-carrying protein in red blood cells, iron is an essential mineral in diet. Iron deficiency in diets therefore lead to anemia amongst other diseases. However, exposure to high doses of iron above 60mg/kg have been reportedly lethal.

Cadmium (Cd) concentration in sampled wastewater according to the study reduced from 1.10±0.00 to below 0.001mg/L. Cd concentration in untreated wastewater was found to be slightly above permissible levels of 1.00mg/L. According to WHO (2011), Cd exposure can trigger dystrophic changes of liver, heart, and kidneys, and also carcinogenic effects.

The concentration of arsenic (As) in treated and untreated wastewater were below detectible limit of 0.001mg/L and permissible limit of 0.1mg/L. As is naturally present at high levels in the groundwater of a number of countries (WHO, 2022), creating a possibility of its presence in untreated oil refinery effluents. As is highly toxic in its inorganic form, posing great threat to public health from arsenic when present in water used for drinking, food preparation and irrigation of food crops. According to WHO (2022), long-term exposure to arsenic from drinking-water and food can cause cancer and skin lesions. It has also been associated with cardiovascular disease and diabetes. In utero and early childhood exposure has been linked to negative impacts on cognitive development and increased deaths in young adults.



The concentration of mercury (Hg) in untreated wastewater were below detectible limit of 0.001mg/L and permissible limit of 0.1mg/L. According to the Water Quality Association, (WQA, 2005), exposures to high levels of metallic, inorganic, or organic mercury can permanently damage the brain, kidneys, and developing fetus. Effects on brain functioning may result in irritability, shyness, tremors, changes in vision or hearing, and memory problems (WQA, 2005).

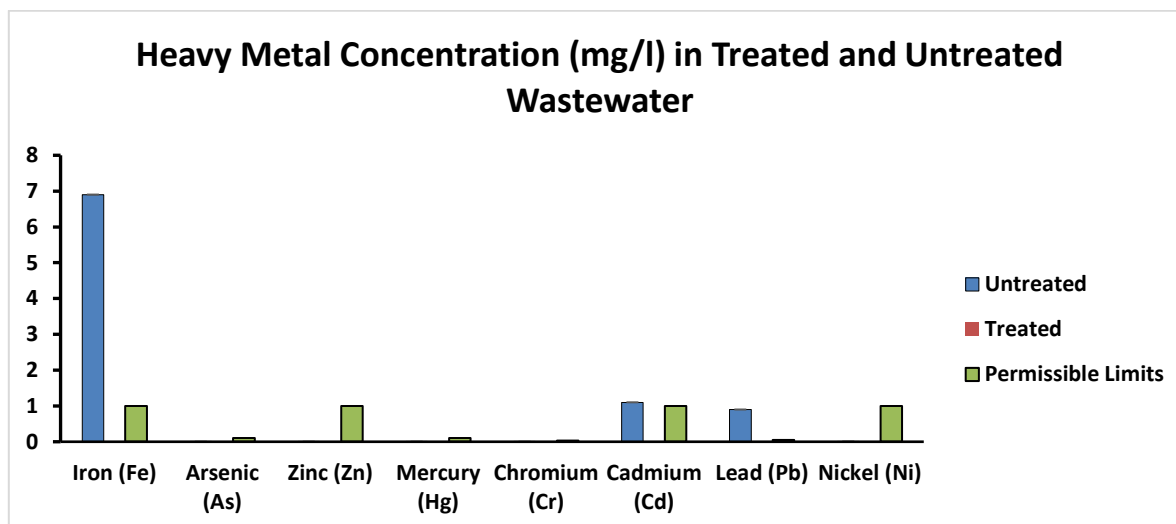


Fig.1 : Concentration of all heavy metals and corresponding tolerable limits

Concentration of nickel (Ni) were found to be below detectable limits of 0.005mg/L for both untreated and treated water, and consequently, below maximum permissible limits of 1.00mg/L. Acute and short-term exposure of Ni on experimental animals have reportedly impaired kidney functions, reduced body weight, hemoglobin, and plasma alkaline phosphatase activity (Nwabueze et al. 2020). Long term exposure of nickel led to retarded growth and death in rats (WHO, 2007). Zinc (Zn) concentration in sampled wastewater were found to be 0.002mg/l for both treated and untreated wastewater, values of which are below tolerable limits of 1.0mg/L. Zinc deficiency have reportedly caused retarded growth in infants and children, delayed sexual development in adolescents, impotence in men and an impaired immune system. Also, zinc deficiency has been implicated in hair loss, diarrhea, eye and skin sore and anorexia in humans and animals (Annapoorna and Janardhana, 2015). However, excess exposure to dietary zinc above permissible limits over a long period causes low immunity, low levels of high - density cholesterol and low copper levels in humans (National Institute of Health (NIH), 2021).

Pearson's correlation as well as analysis of variance (ANOVA) were used to assess the relationship amongst heavy metals concentration (mg/L) of the wastewater samples, and a number of significant correlations were obtained. The statistical analysis in Table 5 showed the correlation matrix of the 7 heavy metals as variables. It is clear from the results that lead was negatively correlated with all the heavy metals except cadmium (with 0.6087), and was not significantly correlated with any of the studied parameters except nickel, to which it was also negatively correlated. Interestingly, all the variables were strongly positively and significantly correlated (at 0.05 level) with each other.



**Table 5** : Pearson's correlation of heavy metals in wastewater

	<i>Arsenic</i> (As)	<i>Zinc (Zn)</i>	<i>Mercury</i> (Hg)	<i>Chromium</i> (Cr)	<i>Cadmium</i> (Cd)	<i>Lead</i> (Pb)	<i>Nickel</i> (Ni)
<b>Arsenic (As)</b>	1						
<b>Zinc (Zn)</b>	1	1					
<b>Mercury (Hg)</b>	1	1	1				
<b>Chromium (Cr)</b>	1	1	1	1			
<b>Cadmium (Cd)</b>	0.42705	0.42705	0.42705	0.42705	1		
<b>Lead (Pb)</b>	-0.45744	-0.45744	-0.45744	-0.45744	0.608728	1	
<b>Nickel (Ni)</b>	1	1	1	1	0.42705	-0.45744	1

The test of significant difference between treated and untreated wastewater was significant at 5 % level. There was no significant difference found between the variables of treated and untreated wastewater. The predictability of heavy metals concentration in wastewater provides a means for easier and faster monitoring of water quality in a location. Nair *et al.*, 2005 concluded that the correlation study and correlation coefficient values can help in selecting treatments to minimize contaminants in groundwater.

### 3.2 Pollution Level of Treated and Untreated Waste Water

Results of the wastewater contamination level are presented in Tables 6 and 7. Contamination factor ( $C_f$ ) results for treated and untreated wastewater are presented in Table 6 while heavy metal evaluation index (HEI) as well as degree of contamination ( $C_d$ ) results are presented in Table 7.

Table 6 shows that every other heavy metals other than iron ( $C_f = 5.9$ ) and lead ( $C_f = 17$ ) had low contamination status in untreated wastewater. However, the very high contamination status of these two heavy metals (iron and lead) greatly reduced to insignificant levels after treatment.

**Table 6** : Contamination Factor ( $C_f$ ) for Untreated and Treated Wastewater

<b>Heavy Metal</b>	<b>Wastewater Sample</b>	
	<b>Untreated</b>	<b>Treated</b>
Iron	5.900	-0.999
Arsenic	-0.990	-0.990
Zinc	-0.998	-0.998
Mercury	-0.990	-0.990
Chromium	-0.967	-0.967
Cadmium	0.100	-0.999
Lead	17.000	-0.980
Nickel	-0.995	-0.995

$C_f < 1 = \text{Low}$ ;  $1 < C_f \leq 3 = \text{Moderate}$ ;  $3 < C_f \leq 6 = \text{Considerate}$ ;  $C_f > 6 = \text{Very High}$

The result of wastewater evaluation index and degree of contamination in Table 7 shows high contamination status for untreated wastewater and considerably low contamination status for treated wastewater. Specifically, the HEI for untreated and treated wastewater were 26.0603 and 0.0823, while the  $C_d$  for untreated and treated

wastewater were 18.0603 and -7.9177, respectively. The high HEI and  $C_d$  values for untreated wastewater are due to high concentration of iron and lead in the untreated wastewater, which greatly reduced after treatment.

**Table 7 : Result of Wastewater Evaluation Index**

Wastewater Sample	HEI*	Degree of Heavy Metal	** $C_d$	Pollution Categories for $C_d$
Untreated	26.0603	High Contamination	18.0603	High Contamination
Treated	0.0823	Low Contamination	-7.9177	Low Contamination

\*HEI= heavy metal evaluation index; \*\* $C_d$ = degree of contamination

### 3.3 Human health risk assessment of treated and untreated waste water

Heavy metals get into humans in a number of pathways via oral, dermal or inhalation, putting humans at risk. It becomes very essential to estimate exposure level to these heavy metals, and this is computed via daily intake estimate contaminated sources. Studying the risk of exposure in toxicological risk assessment for non-carcinogenic and carcinogenic toxicants in wastewater is thus paramount. The health risk assessment of heavy metals for children and adult are presented in Tables 8 and 9, as well as Figures 2 to 4.

#### 3.3.1 Non-Carcinogenic Health Risk of Heavy Metals in Wastewater

The Hazard Quotient (HQ) for the three pathways (ingestion, inhalation and dermal contacts) for Ni, Cd, Pb and Cr for children and adults in order to assess the health risk poses by heavy metals in wastewater is presented in Table 8. Similarly, the hazard index (HI) for non-carcinogenic health risk of heavy metals concentration in wastewater as well as the combined results for HQ and HI are presented in Table 8. Graphical representation of hazard index (HI) for children and adult respectively is presented in Figures 2 and 3.

**Table 8 : Hazard Quotient (HQ) and Hazard Index (HI) values for non-carcinogenic heavy metals in treated and untreated wastewater for Adults and Children**

Pathway	Chromium		Cadmium		Lead		Nickel		
	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated	
Children	Dermal	5.97E-07	5.97E-07	3.94E-03	3.58E-06	6.14E-04	6.82E-07	3.31E-14	3.31E-14
		4.26E-06	4.26E-06	1.41E-03	1.28E-06	8.22E-03	9.13E-06	3.20E-06	3.20E-06
	Inhalation	1.30E-08	1.30E-08	4.08E-05	3.71E-08	9.48E-14	1.05E-16	9.00E-11	9.00E-11
		HI <sub>Children</sub>		4.87E-06	4.87E-06	5.39E-03	4.90E-06	8.83E-03	9.81E-06
Adult	Dermal	1.03E-07	1.03E-07	6.81E-04	6.19E-07	1.06E-04	1.18E-07	5.73E-15	5.73E-15

Ingestion	5.17E-07	5.17E-07	1.71E-04	1.55E-07	9.97E-04	1.11E-06	3.88E-07	3.88E-07
Inhalation	5.28E-09	5.28E-09	1.66E-05	1.51E-08	3.86E-14	4.29E-17	3.66E-11	3.66E-11
HI <sub>Adult</sub>	6.26E-07	6.26E-07	8.68E-04	7.89E-07	1.10E-03	1.23E-06	3.88E-07	3.88E-07

If  $HI < 1$  = no chronic risk; If  $HI > 1$  = non carcinogenic health risk (Yang et al., 2012).

From Table 8, it could be deduced that the major potential risk for children and adults was due to lead via ingestion of untreated wastewater. This is because HQ values for ingestion of untreated wastewater due to lead for children and adults were found to be  $8.22E-03$  and  $9.97E-04$  respectively. Interestingly, all values for HI for children and adults were below 1, indicating that dermal contact, inhalation or ingestion of treated and untreated wastewater poses no chronic risk to humans. It has been reported that the tolerable daily intakes of Pb (0.005 mg/kg) and Cd (0.0004- 0.002 mg/kg) are FAO/WHO recommendations (Udowelle et al., 2017). In another study carried out in Iran, an estimated daily intake of 0.0042 mg/kg was reported by Jawad and Allafaji (2012), higher than the concentration calculated in our present study. However, humans exposed to untreated wastewater are not susceptible to non-carcinogenic health risk when exposed to treated and untreated wastewater, but have a high susceptibility chance to lead poisoning when exposed to untreated wastewater. Generally the daily intake is an estimate of daily exposure to the human population that is likely to be without an appreciable risk of deleterious effect during a lifetime (Udowelle et al., 2017).

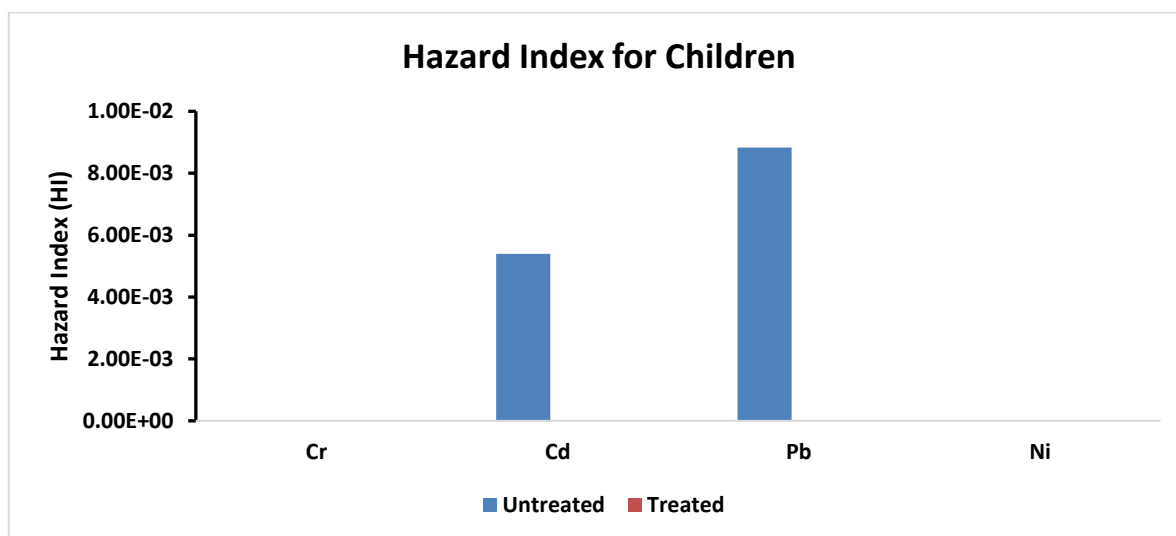


Fig.2 : Hazard Index of untreated and treated wastewater for children

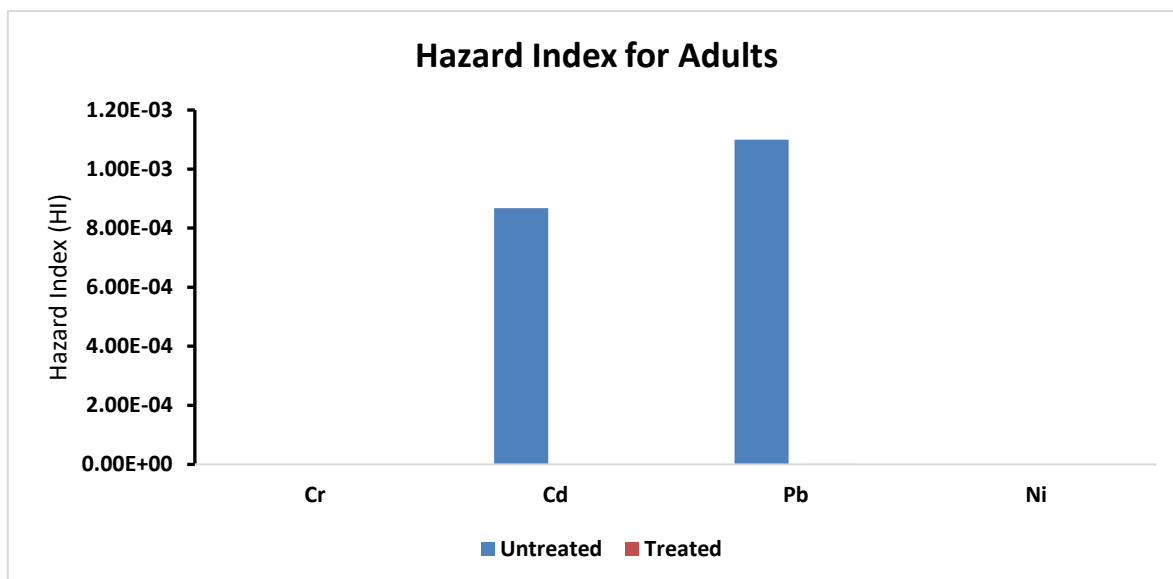


Fig.3 : Hazard Index of treated and treated wastewater for adults

### 3.3.2 Carcinogenic Health Risk of Heavy Metals

The lethal average daily dose (LADD) and cumulative carcinogenic risk ( $R_{total}$ ) for the four carcinogenic heavy metals analyzed in treated and untreated wastewater is shown in Table 9 as well as in Fig.4.

Table 9 : LADD and Cumulative carcinogenic risk ( $R_{total}$ ) values for carcinogenic heavy metals in treated and untreated wastewater for Adults and Children

	Chromium	Cadmium	Nickel	$R_{total}$	Remark
Untreated	1.54E-13	1.69E-10	7.68E-13	1.19E-11	Acceptable
Treated	1.54E-13	1.54E-13	7.68E-13	7.52E-14	Acceptable

*If  $R_{total} < 1E-04$ , not acceptable; If  $R_{total} = 1E-06$ , no significant health risk; If  $R_{total}$  is from  $1E-06$  and below it is acceptable.*

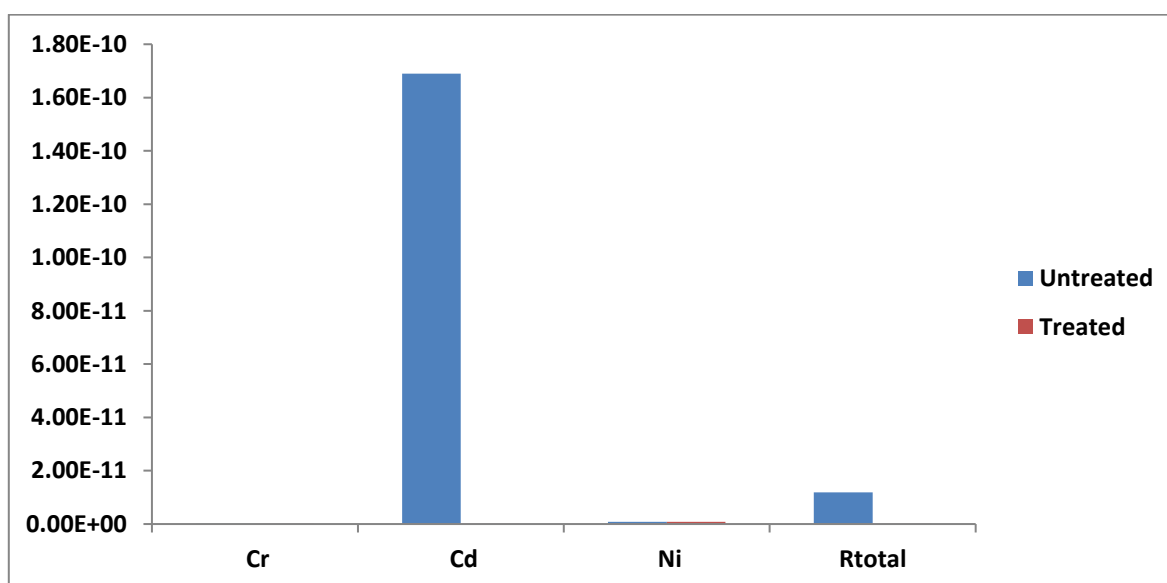


Fig.4 : LADD and Cumulative carcinogenic risk ( $R_{total}$ ) for heavy metals

Though, having chromium as the highest contributor, Table 9 and Fig.4 indicated that LADD and  $R_{total}$  values were within acceptable limits. This was so because  $R_{total}$  values for treated and untreated wastewater were found to be below  $1E-06$ . Also, Udowelle *et al.* (2017) reported similar findings from their research.

Although, the concentration of the metals in this study could be adjudged to be low, the co-contamination of these compounds could likely be of significant public health importance. Co-exposure to metals may lead to either additive or non-additive co-toxicity. In risk assessment, the non-additive effects are of greater concern since contaminants mixture toxicity is greater than the summed toxicity of each of its constituent (Naghipour *et al.*, 2014). Co-toxicity can arise from a variety of interactions, either directly among the co-occurring toxicants or indirectly through the effect of one toxicant on the various process involved in the transport, metabolism and detoxification of the co-occurring toxicant. Estimated incremental lifetime cancer risk associated with metals suggested that numbers of the population likely to get cancer was lower than the acceptable risk level (Gauthiera *et al.*, 2014; Udowelle *et al.*, 2017), the hazard quotient values of the metals were below 1, which indicated no health concern.

#### IV. CONCLUSION

Biological monitoring and health risk assessment of physicochemical parameters of treated and untreated produced water effluent were conducted to rule out the possibility of the presence of harmful chemicals which possess threats to aquatic and terrestrial life. Findings from some key health risk assessment monitored in the produced water indicated they were not harmful. Further, statistical analysis of physicochemical parameters and heavy metal concentration of wastewater showed varying forms of correlation between physicochemical parameters of untreated and treated wastewater as well as heavy

metal concentrations. Overall statistical results evidently provide easier and faster water quality and location monitoring in the future.

Pollution indices as presented shows that most metals have low contamination status in untreated wastewater. However, the relatively high contamination status of the heavy metals greatly reduced to insignificant levels after treatment. Health risk assessment evaluated showed that the major potential non-carcinogenic risk was via ingestion, with lead as the main contributor. Overall non-carcinogenic risk evaluation of wastewater, showed that humans are not susceptible. Similarly, overall values for lethal average daily doses and cumulative carcinogenic risk were within permissible limits.

#### V. ACKNOWLEDGEMENTS

Authors appreciate Dr. Duke Okoro and the entire staff of Dukoria Laboratories, Warri, Delta State, Nigeria.

#### VI. COMPETING INTERESTS

Authors have declared that no competing interests exist.

#### VII. AUTHORS' CONTRIBUTIONS

This work was carried out in collaboration between both authors. Author LETA designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author AJE managed the analyses of the study and the literature searches. Both authors read and approved the final manuscript.

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**Cite this article as :**

L. E. Tudararo-Aherobo, A. J. Egieya, "Public Health Risk Assessment of Treated and Untreated Produce Water Effluent", *International Journal of Scientific Research in Science and Technology (IJSRST)*, Online ISSN : 2395-602X, Print ISSN : 2395-6011, Volume 10 Issue 3, pp. 941-955, May-June 2023. Available at doi : <https://doi.org/10.32628/IJSRST523103173>  
Journal URL : <https://ijsrst.com/IJSRST523103173>