RESEARCH ARTICLE

EVALUATION OF THE EFFECTS OF HEAVY METALS ON WATER FROM ILLEGAL CRUDE OIL REFINERIES: A CASE STUDY OF THREE SELECTED COMMUNITIES IN THE NIGER DELTA REGION, NIGERIA

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ABSTRACT

In order to assess the levels of heavy metals and health concerns associated with the operations of illicit refineries in water, 15 surface water samples were taken from Okernkoko, Peterou-Gbene, and Bille in the Niger Delta region of Nigeria. A number of heavy metal indices, including the Contamination Factor (CF), Pollution Load Index (PLI), Modified Degree of Contamination (mCd), Ecological Risk Factor (ErF), and Geo Accumulation Index (Igeo), were successfully applied in the evaluation of heavy metal contamination in surface water using World Health Organization WHO (2011) and Nigerian Standard for Water Quality NSDWQ (2007) standards. Additional research from WHO and NSDWQ comparisons revealed that the majority of the investigated heavy metals were higher than permissible limits in comparison to the control site. Although the concentration of heavy metals in the aquatic habitats varies amongst the various communities in the area, according to the CV. Additionally, CV contends that there is a connection between the illicit refining activities at the site and the water chemistry changes that result in surface water contamination. According to data from the WHO and the NSDWQ, the majority of heavy metal concentration readings in the study sites exceeded the acceptable limits when compared to those in the control site. According to results of heavy metals indices such as CF and PLI, the surface water in the analyzed site ranges from very slightly contaminated to extremely contaminated. However, ErF and Igeo findings showed that human activities through illegal refiners increase heavy metal concentration, which results in a very high potential ecological risk associated with surface water. Additional mCd results demonstrated that in the studied sites, the surface water has a high degree of contamination. The findings suggest that surface water assessment is required to warn against a decline in water quality in the area.

KEYWORDS

Heavy Metal, Illegal Refineries, Water Pollution, Health Risk

1. INTRODUCTION

Oil discovery has been a wild and adventurous exploration process. More than 1300 different chemicals may be released into the environment as a result of oil and gas exploration and exploitation, according to the Scientific Committee on Health, Environmental, and Emerging Risks (SCHEER) (SCHERR, 2018). Environmental and public health issues are raised by the chemicals linked to oil and gas, such as heavy metals, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), particulate matter, etc. Nigeria is the world’s sixth-largest crude oil exporter, and the Niger Delta region’s reserves total more than 37.4 billion barrels (Orisakwe, 2021). It also contains one of the planet’s most biodiverse ecosystems (Atibiu, 2015; Albert and Kristzina, 2018). The cornerstone of environmental degradation in the Niger Delta for more than five years has been related to the exploration and extraction of crude oil. Illegal crude oil refineries are becoming more prevalent in the area, which is aggravating environmental issues and ecological damage to land and surface water bodies (Tunde and Igoigbe, 2021). The process of artisanal refining starts with the acquisition of stokin crude oil, which is then refined using unauthorized or “bush” refineries and local resources and expertise. Niger Delta region is home to the third-largest mangrove forest in the world, as well as enormous freshwater and saltwater swamps, as well as a wide range of plant and animal species (Anejonu et al., 2015; Kunzer et al., 2021). The region still struggles with oil pollution and contamination, which has a big impact on people despite having a rich, diverse ecology and wildlife (Amnesty International Nigeria, 2009; Ordinioha and Brisibe, 2013). The Gulf of Mexico in 2010, Canadian marine waters, and Prince Williams Sound, Alaska, all reported experienced oil spillage occurrences (Akaninyene et al., 2021). As about 13 million tonnes of crude oil have flowed into the Niger Delta ecosystem since crude oil was discovered there (Orisakwe, 2021). This has also significantly contaminated the land and coastal ecosystem. The region still struggles with oil pollution and contamination, which has a big impact on people despite having a rich, diverse ecology and wildlife (Amnesty International Nigeria, 2009; Ordinioha and Brisibe, 2013). The Gulf of Mexico in 2010, Canadian marine waters, and Prince Williams Sound, Alaska, all reported experienced oil spillage occurrences (Akaninyene et al., 2021). It has been estimated that over 12 million tonnes of crude oil have flowed into the Niger Delta ecosystem since crude oil was discovered there. This has significantly contaminated the land and coastal ecosystem. By releasing petroleum products into onshore and offshore ecosystems, humans and the marine ecosystem have suffered as a result, claim (Tunde and Oluwagbenga, 2021).
Studies conducted revealed that the difficulties faced in managing these adverse effects posed by the activities of illegal refineries have potentially contaminated the water in the immediate environment, which has raised a significant concern in the area (Ojewumi et al., 2017; Akaniyene et al., 2021; Ikekam et al., 2021). Additional research has demonstrated that the suppression of the primary functions of the flora and fauna caused by the buildup of heavy metals in aquatic ecosystems, which makes the water unsafe to drink, is caused by the use of crude oil and other petroleum products (Barenboim et al., 2015; Agoha, 2019). This has a severe adverse effect. This significantly harms lakes, streams, and rivers all throughout the world. In aquatic environment’s water quality is essential for the survival of its flora and fauna as well as the environment’s general health (Emuedo et al., 2014; Hunt et al., 2018). As a result, the mangroves in the Niger Delta have been decimated, and the marshes and rivers are now severely polluted and useless for man’s use (Moses and Tami, 2004). People are already ingesting heavy metals as a result of this process. Following that, the bloodstream transports them to the organs and tissues where they accumulate and pose serious risks to human health due to their toxic, mutagenic, and carcinogenic properties (Atubi, 2005).

Since local crude oil refining has grown to be a significant source of income for those living in the riverine settlements of the Niger Delta, it is crucial to thoroughly assess the quantities of heavy metals in water that has been contaminated by crude oil and the resulting effects on human health. This will serve as a feasibility prototype for further studies in other riverine communities in the region, within the environmental sector and several other sectors, and for clean-up design. This will further provide baseline information on the level of risk faced by the people living within that region and contribute to the development and sustainability of the host communities by generating a chance for a sound, developed economy and cooperation in the Niger Delta region.

2. MATERIALS AND METHODS

2.1 Study Area

The study was carried out in the three main Niger Delta states of Bayelsa, Rivers, and Delta, which are home to the majority of artisanal oil refining operations. The research area is close to the location of the crude oil refining area (point source), which is situated in the freshwater ecosystems of Delta State, Bayelsa State, and the brackish water ecosystem of Rivers State, Nigeria. The region is located between latitudes 4°10’ to 6°20’ North and longitudes 2°35’ to East of the equator. Fig. 1 and Fig. 2 show a map of the study area and the location of an oil spill that contaminated the study zone, respectively.

![Figure 1: Map of the Niger Delta showing the Study Location (Umar et al., 2019).](image1)

![Figure 2: An oil spill contamination map of the research region. (Umar et al., 2019).](image2)

The study is located in an ecosystem with fresh water that has two seasons: the wet and the dry ones (Ainayanaba and Godwin, 2013). The area experiences 1000 to 2000 mm of rainfall on average each year (Nwankwor et al., 2016). Furthermore, Nwankwor et al. (2016) noted that the rainy season lasts from mid-April to early-November and that July and October are the months with the heaviest rainfall. In the research area’s temperature ranges from 26 to 28 °C and its characteristic vegetation is mangrove swamp forest; however, it has been significantly affected by
human activities like exploration, logging, and farming (Eyanware et al., 2020, Eyanware et al., 2022). The coastal region of the Niger Delta has an average monthly wind speed pattern that varies between 0 and 3 m/s, with periods of lower and higher trends noted during the night and evening periods (Edokpa and Nwagha, 2017). The research area’s topography is moderate, with an average elevation of roughly 18 meters above sea level, and there aren’t any ominous hills that tower over the surrounding terrain. Flooding after rain is frequently facilitated by the area’s flood and low-relief qualities (Eyanware et al., 2020). The research area is crossed by a large number of creeks with dendritic drainage patterns, some of which empty their waters into the Atlantic Ocean.

2.2 Water Sampling

A preliminary site study was conducted before collecting samples to guarantee efficient sampling procedures. From the investigated sites and the control sites, a total of fifteen (15) samples taken between 8:00 am to 10.00 am with pre-acid cleaned plastic sample vials or containers at a depth of 25 cm into the water. In order to stabilize the samples’ contents and stop metals from adhering to the container’s surface, two drops of nitric acid were added. The samples were transported to the lab for analysis while being kept in ice-cold packs. Water samples of a known volume of 50 cm³ were digested in a steam bath using a combination of concentrated acids (HNO₃, HCl, and H₂SO₄) in the proportion of 5:3:2. When the mixture became clear or colorless, the digestion was complete. Filtering the samples produced a filtrate that could fill up to 50 cm³ of deionized water. Using a thermal Atomic Elemental Absorption Spectrophotometer, the final filtrate digest was examined for the presence of heavy metals (Model SE-71906). At intervals of five sample runs, a blank was run in the machine to help reduce the error in the analytical data. Three separate analyses for each metal were conducted on each sample, and the findings are shown as mean standard deviation (Sehgal et al., 2012). The APHA criteria were followed during data collection and analysis (APHA, 2012).

2.3 Digestion of Samples

A known volume of 50 cm³ of water samples were digested in a steam bath in a combination of concentrated acids (HNO₃, HCl, and H₂SO₄) in the ratio 5:3:2. The digestion was completed when the mixture turned clear or colorless. The samples were filtered, and the filtrate made up to 50 cm³ with deionized water. The final filtered digest was analyzed for heavy metals using Thermo Atomic Elemental Absorption Spectrophotometer (Model SE-71906). To reduce error in the analytical results, a blank was run at intervals of 5 sample runs in the machine, each sample was analyzed three times for every individual metal, and the results stated as mean ± standard deviation (Sehgal et al., 2012). Data collection and analysis adhered to the APHA standards (2012).

2.4 Heavy Metals Evaluation

With air-acetylene as the fuel source, the heavy metals (Cu, Mn, Pb, Cd, Zn, Fe, Cr, and As) were identified using a flame atomic absorption spectrometer (FAAS) (Ab basi et al., 2020). For the purpose of determining As, however, the flow injection analysis system of an atomic absorption spectrophotometer (FIAS-ASS) utilizing hydride generation technique and cold vapour technique was employed. For the purpose of determining heavy metal concentrations, the Atomic Absorption Spectrophotometer (Perkin Elmer PINAAcle 900 t) was calibrated using predetermined standard quantities of Cu, Mn, Pb, Cd, Zn, Fe, Cr, and As. To reduce error in the results, a blank was performed every five sample runs in the analyses.

2.5 Water Contamination Determination

The level of heavy metals or pollution in water has been determined using a variety of techniques. The level of heavy metal pollution in the contaminated samples was assessed using the Contamination Factor (CF), Pollution Load Index (PLI), Modified Contamination Degree (mCd), Ecological Risk Factor (Erf), and Geo-accumulation Factor (Igeo). The recommended intervals of contamination and pollution descriptions served as the basis for the interpretations of the various evaluation equations.

2.6 Quality Assurance Control

Quality control and assurance procedures were used to guarantee the dependability of the results. In order to protect the integrity of the output, and to prevent any outside interference, the samples were handled carefully. The analysis of blanks and replicate samples was done, and the outcomes were compared to the test results. The (Perkin Elmer PINAAcle 900 t) Atomic Absorption Spectrophotometer was calibrated for the detection of heavy metals using known standard concentrations of Cu, Mn, Pb, Cd, Zn, Fe, Cr, and As. Three repetitions of the measurements were made. Throughout the investigation, acid was used to clean the glass and plastic containers.

2.7 Contamination Factor (CF)

The methodology used to interpret the contamination factor values was taken from (Lacatusu, 2000). The level of heavy metal water contamination was calculated using the contamination factor. The heavy metal concentration to background value ratio is known as the contamination factor is given in equation 1:

\[ CF = \frac{C_m}{Cb} \]

Where;

- \( C_m \) = metal content in contaminated water
- \( Cb \) = background metal concentration in water

<table>
<thead>
<tr>
<th>Table 1: Significance of Contamination Factor/Pollution Load Index (CF/PLI) Intervals</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF/PLI</td>
</tr>
<tr>
<td>&lt;0.1</td>
</tr>
<tr>
<td>0.10-0.25</td>
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<tr>
<td>0.26-0.5</td>
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<td>0.51-0.75</td>
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<tr>
<td>0.76-1.00</td>
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<td>1.1-2.0</td>
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<tr>
<td>2.1-4.0</td>
</tr>
<tr>
<td>4.1-8.0</td>
</tr>
<tr>
<td>8.1-16.0</td>
</tr>
<tr>
<td>&gt;16.0</td>
</tr>
</tbody>
</table>

Source: Lacatusu (2000).

2.8 Pollution Load Index (PLI)

The pollution load index is a gauge of how contaminated an area is overall at a sampling site. Equation 2 was used to calculate the PLI (Hakanson, 1980). Pollution Index (PLI):

\[ PLI = (Cf_1 x Cf_2 x Cf_3 x ... x Cf_n) \times \frac{1}{n} \]

Where;

- \( n \) = number of elements

The contamination factor is denoted by \( Cf \). The baseline metal values and metal concentration in water are represented by the \( Cf \).

PLI = effective instrument for assessing heavy metal contamination. Table 1 above displays the range of pollutants and their relative importance.

2.9 Modified Degree of Contamination (mCd)

To determine the overall impact of heavy metal contamination in an environment, the modified degree of contamination (mCd) was computed using the equation proposed by (Hashibejej et al., 2015). Equation 3 shows how the contamination degree equation was applied.

\[ Cd = \sum_{i=1}^{n} CFI \]

and the Modified Contamination Degree equation applied was equation 4

\[ mCd = i/n \sum_{i=1}^{n} CFI \]

Where;

- \( mCd \) = the modified degree of contamination
- \( C_i = \) contamination factor of the individual metal
- \( n \) = the number of the heavy metals investigated
- \( i \) = ith element

The modified degree of contamination classification by Hakanson was published in 1980 (Abraham and Parker, 2007).

\[ mCd \] values; Sediment quality, \( mCd<1.5 \) nil to low degree of contamination, 1.55<\( mCd<2 \) low degree of contamination, 2.5<\( mCd<4 \) moderate degree of contamination, 4.5<\( mCd<8 \) high degree of contamination, \( 8< mCd<16 \) Very high degree of contamination, \( 16< mCd<32 \) Extremely high degree of contamination, \( mCd>32 \) Ultra high degree of contamination. The concentrations of the various polluters that were found in the samples...
that were evaluated were compared to the suggested reference levels that were regarded safe for public health, such as (WHO, 2011; NSDWQ, 2007).

2.10 Ecological Risk Factor (Erf)

Equation 5 describes the Ecological risk factor (Erf), which was first introduced by Hakanson in 1980 and is the quantitative statement of a given pollutant’s potential ecological risk:

\[ Erf = \frac{Tr \times Cf}{Cf} \]

Where:
- \( Tr \) = toxic-response factor for a specific pollutant and,
- \( Cf \) = contamination factor.

The five categories of terminology used to characterize the ecological risk factor are as follows:
- \( Erf \leq 10 \) (low potential ecological risk), \( 10 < Erf \leq 40 \) (moderate potential ecological risk), \( 40 < Erf \leq 80 \) (considerable potential ecological risk), \( 80 < Erf \leq 160 \) (high potential ecological risk), and \( Erf > 160 \) (very high ecological risk). The risk factor was designed as a diagnostic tool for water pollution control.

2.11 Geo-accumulation index (Igeo)

Equation 6 provides the formula that was used to determine the geo-accumulation index (Igeo) values for the various metals. It was proposed by Muller (1981):

\[ Igeo = 10 \log \left( \frac{Cn}{1.5Bn} \right) \]

Where:
- \( Cn \) = element concentration in the water,
- \( Bn \) = element’s geochemical background or the global average of the element’s concentration in shale.

Seven classes (ranging from 0–6) of the geo-accumulation index to categorize the extent of metal contamination of the water was established by (Muller, 1981). These are: Class 0 = Igeo<0 (practically uncontaminated), Class 1 = 0<Igeo<1 (uncontaminated to moderately contaminated), Class 2 = 1<Igeo<2 (moderately contaminated), Class 3 = 2<Igeo<3 (moderately to heavily contaminated), Class 4 = 3<Igeo<4 (heavily contaminated), Class 5 = 4<Igeo<5 (heavily to extremely contaminated), Class 6 = 5<Igeo (extremely contaminated). Any value below 6 and above is categorized in the open class. The value of an element in a class may be up to several times bigger than its background value. At Muller, the background value used is based on the global average value in shale (mg/kg-1) of the metals identified in the study. The numbers are: Cu = 45, Mn = 850, Pb = 20, Cd = 30, Zn = 95, Fe = 47200, Cr = 90, and As = 13.

2.12 Statistical Analysis.

The test for normality was satisfied by the data collection. To assess the variation between groups of the same samples, descriptive statistics were applied to the heavy metal data in the water from the sampled locations in the study region (ranges, mean, standard deviation). Using the statistical program for social science version 16.0, the mean, the standard deviation error, and the Coefficient of Variation (CV) were calculated while attempting to identify the origin of the heavy metal concentration in the research site’s water (SPSS version 20).

3. Results

Results from Table 2 indicate that the illicit refiners’ waste products have a negative impact on the water quality. A close examination of Fig. 3a to 3h reveals widespread water pollution since the water is heavily slick with crude oil. The region’s already vulnerable environment could further deteriorate as a result of this. Due to the poisonous effluent discharged into the water bodies where these illegal refiners are located, the aquatic species growing in these locations are not safe. The results from the control site show that the heavy metal concentrations of water samples taken from the refinery site were much higher than those from the control site (Table 2).

<table>
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<th>Sample Location</th>
<th>Control Site</th>
<th>Cu</th>
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<th>Pb</th>
<th>Cd</th>
<th>Zn</th>
<th>Fe</th>
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<td>3</td>
<td>0.009</td>
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</table>
3.1 Copper
According to the study, all surface water samples taken from the study site had heavy metal concentrations that were higher than the (WHO, 2011; NSDWQ, 2007) suggested safe maximum limits. The measured value range in the concentrations of Cu in the collected water ranges from 0.010±0.010 to 4.02±0.07 mg/L, which is significantly greater than the Cu value in the control site of 0.01±0.02 mg/L but lower than the Cu value reported in the Bomu and Oginigba Rivers in Rivers State, Nigeria (Marcus and Edori, 2016). Additionally, they were greater than those analyzed by (Edori and Ijama, 2020). Cu is a known essential element required for the efficient breakdown and building of cells, but high concentrations in food and water can irritate the neurological system and lead to depression as well as necrosis in hepatic and renal cells (Edori and Kpee, 2020). Due to the inhibition of enzyme activity, anemia, and blood dilution are caused by high concentrations of Cu (Marcus and Edori, 2016). Fig. 3a displays a graphical representation of Cu in comparison to standards from WHO, (2011) and NSDWQ, (2007). Manganese (Mn) concentrations range from 0.001±0.001 to 0.64±0.008 mg/L in the study region.

3.2 Manganese
The majority of the observed levels of Mn in every studied location were higher than the limits of 0.0001 mg/L and 0.006 mg/L imposed by the (NSDWQ, 2007; WHO, 2011). But higher than the value in the control site of 0.00±0.02 mg/L. The data on the concentrations of Mn in the study are consistent with the levels seen in the Drini Bardhe River (Haxhibeqiri et al., 2015). And the study in Orashi River, Rivers State, Nigeria (Nwankwoala et al., 2017; Odoemelam et al., 2019). In natural habitats like water, the metal Mn is widely distributed. Its sources in water can either be manmade or natural (Tirkey et al., 2012; Puri et al., 2015). In Fig. 3b, Mn is represented graphically in comparison to standards from WHO, (2011) and (NSDWQ, 2007).

3.3 Lead and Arsenic
The Lead (Pb) and Arsenic (As) values found in the study sites were relatively close in concentration. As ranges from 0.02±0.10 mg/L, while Pb is between 0.00±0.18 mg/L. 0.01 mg/L of lead (Pb) is the recommended value of (WHO, 2011; NSDWQ, 2007). The level of Pb in the current study is lower than the range of 0.55–0.06 mg/L at the control site. The amount of As is, however, 0.01–0.03 mg/L higher than the value at the control site. The result from the study revealed that Pb concentration values are higher than allowed limits. This is consistent with the assessed level of lead (Pb) in surface water from the River Ijana in Warri (Obiwakem, 2013). The results of the investigation showed that the amounts of heavy metals were higher than the recommended limits, with Pb having the greatest concentration (WHO, 2011). Additionally, Pb levels was evaluated in water samples from the communities of Nembe, Ikiri, and Okpare (Emeue et al., 2014). And Pb, As in subsurface water samples from the Umuehui community (Ejike et al., 2017). Further result from their findings showed that Pb and As levels in drinking water were higher than suggested limits (WHO, 2011; NSDWQ, 2007). However, subsequent analysis of the study’s results showed that the levels of Pb in samples 1 and 2 from River State, 3, from Delta State, and 3, from Bayelsa State, were all within the acceptable range. Though all values were seen to be lower than those of (Nnadi et al., 2021). They were also either found to be within the same range or lower than the values observed in several Nigerian water bodies. Fig. 3c and 3g provide a graphical representation of Pb and As in comparison to (WHO, 2011; NIS, 2007) standards. The presence of crude oil from illicit refineries’ waste products and the indiscriminate dumping of metal trash are the two main causes of the study area’s elevated Pb and As concentration.

3.4 Cadmium
The maximum allowable level for any drinking water is 0.003 mg/L, which is within the range of values but higher than the control sites 0.022 mg/L. The content of cadmium (Cd) in all sampled locations ranged from 0.0012±0.010 to 0.052±0.008 mg/L. This suggests that the Cd levels in the study sites were within acceptable bounds which correspond to the research carried out by (Inasmun and Egai, 2013). Fig. 3d displays a graphical comparison of the Cd concentration with the WHO, (2011) and NSDWQ, (2007) standard. Although the greater levels of Cd in human, animal, or plant tissue have the tendency to infect essential amino acids and accumulate in the proximal tubular cells at very high concentrations, which further results in kidney and lung damage. Increased levels of Cd can also result in liver dysfunction, a decrease in the weight of newborns, and premature birth in pregnant mothers (Ejike et al., 2017). Other diseases linked to Cd exposure include procreative disorders, behavioral issues, cardiac and vascular neurology, hematological, and damage to hepatocytes and other key bodily organs (Eucharia et al., 2016).
3.5 Zinc

Zinc (Zn) concentrations in the study region range from 0.001±0.001 to 0.029±0.001 mg/L which is significantly higher than the Zn level of 0.000±0.001 mg/L in the control site but less than the permissible limit of 3 mg/L WHO, (2011) and NSDWQ, (2007). Similar to this, the concentrations from the sampled site are within the value range seen in a similar study conducted in the Okrika and Ogi-Bolo Areas of Rivers (Nwankwoala et al., 2017). But lower than those of Edagberi Creek, Engenni River (Edori and Iyama, 2020) and Agubiri Community in Southern Ijaw L.G.A. (Imaseun and Egai, 2013). Zn is a necessary element in the human system due to the various biochemical and metabolic functions it performs in body tissues and cell proliferation. Although these symptoms are temporary, the presence of concentrated quantities of Zn may cause intestinal irritation, nausea, anorexia, depression, illness, and cough (Ngaram et al., 2017; Rastmanseh, 2020). Zn is known to cause water to taste bitter and become more opaque, especially in home water with an alkaline pH, even though there has not been any experimental or scientific evidence of physiological concerns when Zn is taken up at doses higher than 3 mg/L (Teppe, 2014). In Fig. 3e, Zn is graphically represented in comparison to WHO, (2011) and NSDWQ, (2007).

3.6 Iron

The iron (Fe) concentrations in the research region range from 0.0001±0.002 to 8.56±0.17 mg/L, while the recommended value for Fe is 0.3 mg/L (WHO, 2011; NSDWQ, 2007). The results of this study’s Fe analysis are comparable to those of another study done in Nigeria by (Kwatamshuwa et al., 2019), but they are not the same as research done by (Nwankwoala et al., 2017). The results obtained from all sampled sites are either slightly above (0.009 mg/L) or slightly below (WHO, 2011). And the permissible limits of 0.3 mg/L (NSDWQ, 2007). While Fe is thought to be a necessary component of the human body, there is no danger to human health from a higher Fe concentration. However, it causes rusty and brownish coloration, incrustation, and stains clothes. In Fig. 3f, Pb levels are graphically represented in comparison to WHO, (2011) and NSDWQ, 2007.

3.7 Chromium

Chromium (Cr) concentrations in surface water range from 0.02±1.31 mg/L in the study areas, which is somewhat more than the 0.05 mg/L permissible limit for the WHO and NSDWQ, respectively. According to research done in Nigeria’s Edo State, the Cr levels in the Ekehuan River ranged from 0.03±0.05 mg/L (Aganmwonyi et al., 2021). In other words, the concentration of chromium (Cr) remained within the allowed range of (NSDWQ, 2007). Thus, their concentrations were at their highest because Cr did not vary noticeably. In a related study of an oil-polluted site, it was noted that the mean Cr concentration recorded was 4.2 mg/L. This was attributed to the pollution caused by spills from illegal refineries (Bucharia et al., 2016). Figure 3g depicted a graphic comparison of Cr levels to WHO, (2011) and NSDWQ (2007) standards.
In Tab 3.3.1   Contamination Factor (Cf)

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3.8

from reporte

Cu

Zn

Cd

Fe

As

1.23

0.362

0.007

0.046

0.022

0.362

0.034

2.10

0.777

0.467

0.022

0.007

12.39

0.362

2.642

3.26

1.552

1.355

0.127

747.33

26.83

27.06

95.65

2.642

798.32

26.72

26.77

CV %

Table 3: Descriptive Statistics of Heavy Metals Concentration in Water Samples from the Studied Sites.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Mean value</th>
<th>Standard deviation</th>
<th>CV %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>2.10</td>
<td>0.281</td>
<td>747.33</td>
</tr>
<tr>
<td>Mn</td>
<td>0.077</td>
<td>0.287</td>
<td>26.83</td>
</tr>
<tr>
<td>Pb</td>
<td>0.046</td>
<td>0.170</td>
<td>27.06</td>
</tr>
<tr>
<td>Cd</td>
<td>0.022</td>
<td>0.023</td>
<td>95.65</td>
</tr>
<tr>
<td>Zn</td>
<td>0.007</td>
<td>0.265</td>
<td>2.642</td>
</tr>
<tr>
<td>Fe</td>
<td>12.39</td>
<td>1.552</td>
<td>798.32</td>
</tr>
<tr>
<td>Cr</td>
<td>0.362</td>
<td>1.355</td>
<td>26.72</td>
</tr>
<tr>
<td>As</td>
<td>0.034</td>
<td>0.127</td>
<td>26.77</td>
</tr>
</tbody>
</table>

Statistical Analysis Result from Heavy Metals

Table 3 displays the data from the CV of heavy metals in the study area, which showed that the CV of Cu, Mn, Pb, Cd, Zn, Fe, Cr, and As were above 60%. As seen in (Table 3, Fig. 4), Fe (798.32%) had the highest Coefficient of variation (CV), followed by Cd (747.33%), and finally Mn (95.65%). For the apportionment of heavy metal sources, famous researchers from around the world have successfully employed statistical analysis CV (Akaninyene et al., 2021; Wang et al., 2021; Eyankware et al., 2022). With the exception of Mn, Pb, Zn, Cr, and As, which ranged from 26.83%, 27.06%, 2.642%, 26.72%, and 26.77%, respectively, the conducted study showed that the CV of Cu, Fe, Cd, and Fe pollutants were above 60%, demonstrating the diverse range of these metals’ (Cu, Mn, Pb, Cd, Zn, Fe, Cr, and As) variations and the significant impact of human activity on their accumulation in water (Ulaaka and Eyankware, 2021; Eyankware et al., 2021). In particular, this shows that the heavy metals Cu, Mn, Pb, Cd, Zn, Fe, Cr, and As that were identified in the soil of the research site were introduced by the crude oil spillage (artificial sources). Because there are no other obvious significant activities taking place in the research site aside from fishing, as reported by residents, crude oil spill is mentioned as a source of pollution. This finding is consistent with the presence of heavy metals in the area stemmed from the same source (Nwanwokwa et al., 2017, Edori and Iyama, 2020, and Akaninyene et al., 2021).

Heavy Metals Estimation Pollution Indices Pollution in Water

3.3.1 Contamination Factor (Cf)

In Table 4 below, the contamination factor (Cf) for heavy metals in the research area is provided. When the contamination data from the various stations in all of the sampled locations are interpreted using (Lacatusu, 2000), it is revealed that the water samples were only very slightly contaminated with Cu in locations 6, 9, 12, and 14, slightly contaminated in locations 3, 11, and 13, moderately contaminated in locations 4, 6, and 7, and severely contaminated in locations 2, 5, and 10, respectively. The results for Mn demonstrates that samples were lightly contaminated in sampled locations 1, 5, and 13, moderately contaminated in sampled locations 1, and 4, severely contaminated in sampled locations 4, and 9, and very severe in contaminated sampled locations 9, 12, 14, and 15, slightly polluted in sampled locations 8 and 15, moderately polluted in sampled locations 2, 3, and 6, and excessively polluted in sampled locations 10 and 11.

The results obtained for Pb indicate very mild contamination at sampled locations 9, and 15, severe contamination at sampled locations 1, 5, and 14, and only slight contamination at sampled locations 8, and 12. There is also severe contamination at sampled locations 13, 4, and 12. The result obtained showed mild contamination in sampled locations 8, moderate contamination in sampled locations 11, very severe contamination in contaminated sampled locations 12, slight pollution in sampled locations 1 and 4, severe pollution in sampled locations 2, 3, 5, 6, and 10, and excessive pollution in sampled locations 13. With the exception of sample 9, which exhibits very minimal pollution, the Zn value obtained showed that all of the investigated areas were polluted.

Analysis of the results obtained for Fe reveals very slightly contaminated in tested locations 8, 12, and 13, slightly contaminated in sampled locations 3, 6, 7, 10, 11, and 14, moderately contaminated in sampled locations 8, and 9 and moderately polluted in sampled location 1. Very
Table 4: Contamination Factor Analysis of Heavy Metals Contamination of Water Samples from the Different Study Sites.

<table>
<thead>
<tr>
<th>Heavy metal</th>
<th>No of sampled locations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.60 0.51 0.12 0.47</td>
</tr>
<tr>
<td>Mn</td>
<td>0.32 3.69 3.61 0.51</td>
</tr>
<tr>
<td>Pb</td>
<td>0.68 1.5 2.0 4.25</td>
</tr>
<tr>
<td>Cd</td>
<td>1.59 4.41 6.25 2.0</td>
</tr>
<tr>
<td>Zn</td>
<td>0.00 0.00 0.00 0.00</td>
</tr>
<tr>
<td>Fe</td>
<td>3.93 5.58 0.096 6.00</td>
</tr>
<tr>
<td>Cr</td>
<td>0.16 2.29 1.796 1.29</td>
</tr>
<tr>
<td>As</td>
<td>5.25 N/A 2.25 N/A 1.5 N/A 3.0</td>
</tr>
</tbody>
</table>

Table 5: Contamination Factor, Pollution Load Index and Modified Contamination Degree of Water Samples from the Different Study Sites.

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>No of Sampled Locations</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLI</td>
<td>0.214 16.101 0.201 1.431</td>
</tr>
<tr>
<td>mCd</td>
<td>0.112 0.173 0.145 0.165</td>
</tr>
</tbody>
</table>

Table 6: Ecological Risk Factor of the Various Metals at the Sample Stations.

<table>
<thead>
<tr>
<th>Heavy Metals</th>
<th>Contamination factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>11.755</td>
</tr>
<tr>
<td>Mn</td>
<td>NA</td>
</tr>
<tr>
<td>Pb</td>
<td>45.9</td>
</tr>
<tr>
<td>Cd</td>
<td>577.77</td>
</tr>
<tr>
<td>Zn</td>
<td>0.0068</td>
</tr>
<tr>
<td>Fe</td>
<td>NA</td>
</tr>
<tr>
<td>Cr</td>
<td>11.328</td>
</tr>
<tr>
<td>As</td>
<td>90.0</td>
</tr>
</tbody>
</table>

3.3.2 Contamination Factor, Pollution Load Index and Modified Contamination Degree of Water Samples

Table 5 and Fig. 5a below indicate the Contamination Factor, Pollution Load Index, and Modified Contamination Degree of water sample from the several sampled locations in the research area. When the pollution load index values from the studied locations were compared to the intervals of pollution index evaluation, it was found that every place was between very slightly and very excessively polluted with heavy metals (Hakanson, 1980). This assumption is made on the basis of the fact that all of the results fell into the category of (0.1 PLI < 16.0) which denotes a heavy metal-polluted environment. The examination of the heavy metals in the water test findings based on the proposed modified contamination degree evaluation revealed that sampled locations 1, 6, 12, and 15 show very slight contamination. Sampled locations 3, 8, and 9 exhibit slight contamination, sampled locations 5, 10, and 15, moderate contamination, and sampled location 4 exhibits slight pollution, while sampled location 16, 10, and 1 exhibit extreme pollution. (Abraham and Parker, 2007). A measurement of the level of general pollution in surface water is intended to be provided by the mCd. The categorization for the interpretation and description of mCd, all values obtained at all sampled locations in all of the individual stations evaluated fall between the ranges of nil to high degree of contamination (4 ≤ mCd<8), as shown in Table 5. This is in accordance with high level of contamination in research done by (Unyime, 2013).

3.4 Ecological Risk factor

The ecological risk index (Erf), which is used to indicate the potential ecological risk for a specific surface water sample, is the total of all Erf values. As shown in Table 6 and Fig. 5b below.

The results for Cu in the investigated sites indicate low potential ecological risk. The evaluated sites had minimal to nil ecological potential risk for Mn and low to moderate ecological potential risk for Pb levels. The water was mostly uncontaminated for Fe, whereas Cd readings ranged from low to very high in terms of possible ecological risk. However, Cr also exhibits low potential ecological risk, whereas As exhibits low to considerable potential ecological risk. This implies that according to the Erf values in Table 6, 100% of the water samples taken from the study locations are thought to be within the range of low potential ecological risk to high potential ecological risk (40-Erf<80 Erf>320). The research's findings are comparable to the conducted in Nigeria by (Unyime, 2013) but not in line with that of (Trilkey, 2012).
3.5 Geo-Accumulation Index (Igeo)

Results of the mean geo-accumulation index (Table 7 and Fig. 6) show the following pattern: Fe > Cu > Mn > Cr > Pb > Cd > Zn > As (Figure 6). Fe, Cu, Mn, and Cr are classified as being in class 6 (highly contaminated) by Muller (1979). Pb is classified as being in class 3 (moderately to substantially contaminated), and Cd, Zn, and As are classified as being in class 2 (moderately contaminated). As a result, it can be inferred that the water samples in the research area are either very contaminated or only mildly contaminated. The findings of this study are in agreement with research done in Ghana by (Samuel et al., 2022) and in Nigeria by (Unyime et al., 2015). But not in line with research done in Nigeria by (Orisakwe, 2016; Edori, and Kpee, 2017). Hence, it was observed that the largest heavy metal sinks in the marine ecosystem are located in the uppermost superficial water, making the geo-accumulation significant in terms of weight per square meter. Following their entry into surface water, these heavy metals often pose risks to aquatic life due to their re-suspension into the water column as a result of geochemical cycling, bioaccumulation in benthic organisms that consume substrate nutrients, and biomagnification through the aquatic food web.

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Contamination factor</th>
<th>Okonkolo</th>
<th>Peterou-Gbene</th>
<th>Bille</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>2.9356</td>
<td>1.9734</td>
<td>2.4465</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.9723</td>
<td>2.888</td>
<td>2.6409</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.7047</td>
<td>0.5813</td>
<td>0.9725</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.7123</td>
<td>0.3579</td>
<td>0.8116</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.9660</td>
<td>0.0539</td>
<td>0.3531</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>6.0092</td>
<td>4.3624</td>
<td>2.5770</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>2.5705</td>
<td>2.3975</td>
<td>1.4754</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>0.6191</td>
<td>0.5399</td>
<td>0.0839</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 6:** Seasonal changes in the Geo-accumulation Index of heavy metals in the research area's surface water

**4. Conclusion**

By comparing the level of heavy metal concentration to the WHO and NDSWQ standards, using statistical analysis indexes (graphs and diagrams), and heavy metal indices like Cf, PLI, mCd, Ef, and Igeo, the research that has been presented has helped in evaluating the status of...
heavy metal pollution of water from illegal crude oil refineries in selected communities within the Niger Delta region. According to the study's findings, water near where oil exploration and production activities are conducted—as well as oil spillages—is frequently contaminated. As crude oil contamination can gradually increase the content of heavy metals such as Cu, Mn, Pb, Cd, Zn, Fe, Cr, and As. Similar to this, the mean levels of heavy metals including Cu, Mn, Pb, Cd, Zn, Fe, Cr, and As range from 0.034 to 12.39. Based on the geographical distribution of heavy metals in surface water, it was determined that the study sites had a higher concentration of heavy metals than other communities in the area. This can be a result of illegal refineries operating in the studied sites. With the exception of Mn, Pb, Zn, Cr, and As, the CV result showed that Cu, Fe, and Cd Fe were above 60%. Indicating that even though a significant amount of crude oil has been spilled into the Niger Delta region, the concentration of heavy metals in the aquatic habitats may differ across various localities in this area. Further investigations using heavy metals indexes such as C and Zn and Cu have C values ranging from very slightly to very severely polluted (<0.1 to 0.76 and 1.00), whereas Pb, Cr, and As have values ranging from severe to extremely polluted, and Mn and Fe are among the very severely to excessively polluted. Results from C, PLI, and Cd indicated a link between anthropogenic activities in the region and those of illegal refineries. Findings from C, PLI and Cd indicate that surface water is contaminated, and fewer than 15 surface water samples were collected overall. This shows that the potential ecological risk is very high. The amounts of Cu, Mn, Cr, Pb, Cd, Zn, and As in the study region are all moderately to very contaminated, according to Igeo results. All analyses reveal that residents have a significant level of heavy metal buildup. The study found that both surface water is impacted by human activity in the study region. Because of the significant amount of oil being split in the area, the results of the current study suggest that residents in the Niger Delta region may be in danger of heavy metal toxicity.

Hence, it is recommended that effective techniques should be devised to reduce the frequency of oil spills in order to lessen the degree of exposure to heavy metals and the risk of toxicity in the Niger Delta region. Oil spills should be contained and cleaned up more quickly. The government should also set up a facility where the local population may be evaluated and detoxified of heavy metals as appropriate because of the vast range of harmful health impacts that heavy metals can have on people. It is also advised to do a comprehensive analysis of the Niger Delta's heavy metal toxicity danger.

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