



## **Assessment of Heavy Metal and Polycyclic Aromatic Hydrocarbon (PAH) Levels in Drilling Fluids and Effluents from Niger Delta Oil Fields**

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Received: February 2, 2025 / Accepted: April 4, 2025

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### **Abstract**

The Niger Delta region, located in southern Nigeria, West Africa, is a significant hub for oil production. However, drilling activities in this region generate substantial amounts of waste effluents, posing environmental and health risks. This study investigates the concentrations of heavy metals and polycyclic aromatic hydrocarbons (PAHs) in drilling fluids and their effluents from Niger Delta oilfields. A total of 14 samples of produced water were collected from seven different oil drilling locations and analyzed for heavy metals and PAHs using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and Gas Chromatography-Mass Spectrometry (GC-MS), respectively. The results revealed elevated levels of some heavy metals and PAHs, exceeding international standards. Specifically, the mean concentrations of Aluminum (Al) (0.522 mg/L), Boron (B) (1.004 mg/L), and Iron (Fe) (2.359 mg/L) exceeded the WHO's acceptable threshold limits for metals in water. In contrast, Barium (Ba), Cobalt (Co), Strontium (Sr), and Zinc (Zn) were within acceptable limits. Notably, some heavy metals were detected in the effluents but not in the drilling fluid. These included Beryllium (Be) (1.365 mg/L), Chromium (Cr) (0.094 mg/L), Manganese (Mn) (0.085 mg/L), and Thallium (Tl) (0.016 mg/L). Conversely, Antimony (Sb), Arsenic (As), Cadmium (Cd), Molybdenum (Mo), Nickel (Ni), Selenium (Se), Titanium (Ti), and Vanadium (V) were not detected in either the drilling fluid or the effluents. The analysis of PAHs in produced water samples revealed concentrations that exceeded EU

standards by a significant margin, whereas the control sample showed relatively low concentrations. This study highlights the substantial environmental and health risks associated with heavy metal and PAH pollution in Niger Delta oilfields. These risks include potential harm to aquatic life, soil and groundwater contamination, and adverse human health effects. The findings emphasize the need for enhanced regulatory measures, improved waste management practices, and the adoption of eco-friendly drilling fluid alternatives. This study contributes to a better understanding of the impact of heavy metal and PAH pollution in Niger Delta oilfields and provides valuable insights for policymakers, oil companies, and stakeholders on the necessity of sustainable environmental management practices. Recommendations include regular monitoring, effective waste disposal strategies, and personnel training programs to mitigate heavy metal and PAH pollution in the region.

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**Keywords:** Drilling mud effluents, heavy metals, petroleum, hydrocarbon, environment

## 1.0 Introduction

Drilling mud is generally used in the upstream oil and gas industry and is a complex mixture consisting of solids and liquids, as well as base oils and brines (Osuji *et al.*, 2013). Drilling fluid, therefore, is typically a combination of water, clay, weighting materials, and a variety of chemicals to adjust the properties of the fluid to meet the requirements of each well. The fluid has several roles throughout the drilling process, including removing cuttings, cooling and lubricating the drill bit, and carrying various chemicals down the borehole. The key to making the rotary drilling system work is to circulate drilling fluid (or drilling mud) continuously down the hole through the drilling pipe and out through the annulus back to the surface. The fluid is cleaned by passing over a shale shaker, where unwanted solids are removed, and the resultant cleaned fluid is then re-injected into the well (Onwukwe *et al.*, 2012).

Drilling operations are generally classified into offshore and onshore drilling. Some environmental challenges have been associated with drilling fluids. A variety of wastes are generated in the drilling of oil and gas wells, including drill cuttings and used drilling fluids.

The process of mud mixing and treatment is generally recognized as a major source of pollution, resulting in various pollutants such as barium, mercury, cadmium, diesel (from lubricants, spotting fluids, and oil-based mud cuttings), arsenic, and formaldehyde (from biocides). The broader environmental problems faced by the oil and gas exploration and production industry are evident both at local and international levels. The disruption of the ecological balance through drilling operations occurs through surface discharge of pollutants from various activities affecting the environment. Environmental management of drill sites is a serious challenge in combating drilling pollution, both onshore and offshore (Adaobi *et al.*, 2016).

Therefore, the discharge of untreated drilling effluents into seas, rivers, or land constitutes a serious health hazard and is detrimental to agriculture and fish. Water sources can also become contaminated. However, the most significant concern relates to the degradation of land, air, and water around the drill sites. Hence, there is a need to conduct a comprehensive risk assessment when deciding the type of drilling fluid method to use, considering its environmental

impact. Drilling waste can have different potential impacts depending on where it is discharged.

Many of the additives used in drilling mud are considered toxic and are regulated. Drilling mud and cuttings can be oil-based (OBM) or water-based (WBM) and are associated with changing concentrations of hydrocarbons and heavy metals. Drill cuttings have been observed to contain a wide range of organic and inorganic traces, especially when oil-based mud is used (Onwukwe *et al.*, 2012). Spent-up drilling fluids and cuttings account for about 2% of the entire waste volume, while other associated wastes, like produced formation water, contribute over 90% of the total waste volume. One of the immediate physical environments that suffer the direct impact of drilling waste disposal is both onshore and offshore (Ahammad *et al.*, 2017). The onshore environment includes swampy, freshwater, and dry land areas, all of which have their peculiar features and ecological characteristics. Although drilling mud used for drilling onshore oil wells is disposed of in reserve pits, due to the large volume of drill waste, much of the mud and cuttings can end up in the adjacent soil and water bodies.

## 2.0 Methodology

### 2.1 Study Area

Eastern Obolo Local Government Area (LGA) is a coastal area in Akwa Ibom State, Nigeria, bordered by the Atlantic Ocean to the south, Mkpato Enin Local Government Area to the north, Onna to the northeast, Ikot Abasi to the west, and Ibeno Local Government Area to the southeast (Ndu *et al.*, 2018). The area lies between latitudes 4° 28' and 4° 53' North and longitudes 7° 50' and 7° 55' East, and is situated between the Imo and Qua Iboe River estuaries (Udo *et al.*, 2015). The region features several rivers, including the Qua Iboe River, Imo River, and Okoro River. The landscape is characterized by coastal plains, mangrove swamps, and sandy beaches, with a

total landmass of approximately 117,008 square kilometers and an estimated shoreline of about 184 km (Ajayi *et al.*, 2013).

As of 1996, the population was around 30,000, with the Obolo ethnic group making up 75% of the population, followed by Ibibio and Ibo (Ekeocha, 2017). However, another source estimates the population to be around 100,361 (National Population Commission, 2006). The people of Eastern Obolo are predominantly fishermen, with over 65% involved in active fishing (Akwa Ibom State Government, 2020). The area has abundant mineral deposits, with onshore and offshore oil wells at Elek-Okpooñ, Iko, Otunene, Emeroke, Ikonta, and Obianga (Ekeocha, 2017). Forest reserves include mangrove, iroko, raffia, rubber, kolanut, coconut, peas, and mango. The economy is primarily based on fishing, agriculture, and trade (Ndu *et al.*, 2018).

The control sample was obtained from Itu. Itu LGA is located in the south-south region of Nigeria, covering an area of approximately 606 km<sup>2</sup>. It shares borders with Uyo, Ikono, Ibiono Ibom, and Ini LGAs. The area has a tropical monsoon climate with two distinct seasons: wet and dry. The entire study area is located in the Niger Delta region of Nigeria.

### 2.2 Materials

Produced water was obtained from a fresh oil well through Oil Company 'A'.

Ocean and river water effluent: Water samples were obtained from six different locations in the ocean and river. The control water sample was obtained from Itu LGA in Akwa Ibom State. Concentrated HNO<sub>3</sub> was used to prevent the reactivity of other compounds.

### 2.3 Methods

#### 2.3.1 Collection of Samples

Water (H<sub>2</sub>O) sample was collected in 6 (six) different locations. Two (2) different locations in

the same ocean, four (4) different rivers, three (3) of the rivers empty into the ocean and vice versa. One of the samples (the control) was collected in a river far apart and does not empty into the ocean. Sample one (1) was collected at location (L1)-Lat/Lon: 4.508093° /7.727900°, sample two (2) was collected at location (L2) -Lat/ Lon: 4.508093° / 7.727900°, sample three (3) was collected at location (L3) -Lat/ Lon:4.508347 ° / 7.727900 °, sample four (4) was collected at location (L4)-Lat/ Lon: 4.515646 ° / 7.769593 °, sample five (5) was collected at location (L5)-Lat/ Lon:4.513401 ° / 7.753092° and the control sample (6) was collected at location (R) - Lat/Lon:5.152504° /7.947876 °.

**2.3.2 Handling of Samples:** Sample storage and preparation of composite samples were done according to standard and best practice.

### 2.3.3 Elemental Analysis using inductively Coupled Plasma-Optical Emission

**Spectroscopy (ICP-OES):** The concentrations of heavy metals were analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES).

#### 2.3.3.1 Analysis Procedure

The Agilent 720-ES with megapixel CCD detector was used which provided simultaneous measurement while the Agilent SPS3 auto sampler was used for sample introduction. Agilent Expert II Software was used to control the

instrument and acquire data. Calibration and Quality Control (QC) solutions were prepared from the following reference material:

1. Agilent Calibration Mix Majors (6610030700).
2. Deionized water from Elga B114 Wall

### Mounted Deionizer System

Appropriate concentrations range of working standards from the multi-elements stock standard were prepared through serial dilution method. A new worksheet was created using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) Expert software into which was programmed the individual sample codes as well as the method with the parameters in Table 1. After the instrument was programmed, the calibration curves were then obtained by running the standards and then the samples were also analyzed according to the sequence specified in the sequence parameters of the newly created worksheet.

The correlation coefficient (r) was calculated using the formula for the Pearson Product-Moment Correlation Coefficient (r):

$$r = \Sigma[(x_i - \bar{x})(y_i - \bar{y})] / (\sqrt{\Sigma (x_i - \bar{x})^2} * \sqrt{\Sigma (y_i - \bar{y})^2})$$

where r = Pearson correlation coefficient,  $x_i$  = individual data points in List 1 (x),  $\bar{x}$  = mean of List 1 (x),  $y_i$  = individual data points in List 2 (y),  $\bar{y}$  = mean of List 2 (y) and  $\Sigma$  = summation symbol, indicating the sum of the values

**Table 1:** Instrument conditions

PARAMETER	SETTING
Power	1 Kw
Plasma gas flow	15 L/min
Auxiliary gas flow	15 L/min
Spray chamber type	Glass cyclonic
Torch	Standard axial torch
Nebulizer type	Sea Spray
Nebulizer gas pressure	220 kPa
Pump speed	220 kPa
Pump speed	15 rpm

Sample uptake	30 s
Replicate read time	30 s
Number of replicates	2
Sample delay time	20 s
Stabilization time	15 s
Rinse time	10 s
Fast pump	On

### 3.0 Results and Discussion

The mean concentrations of various heavy metals content for pentaplicate samples water from the study area, produced water control, WHO and EGASPIN Standards are as presented in Table 2 and Figure 1.

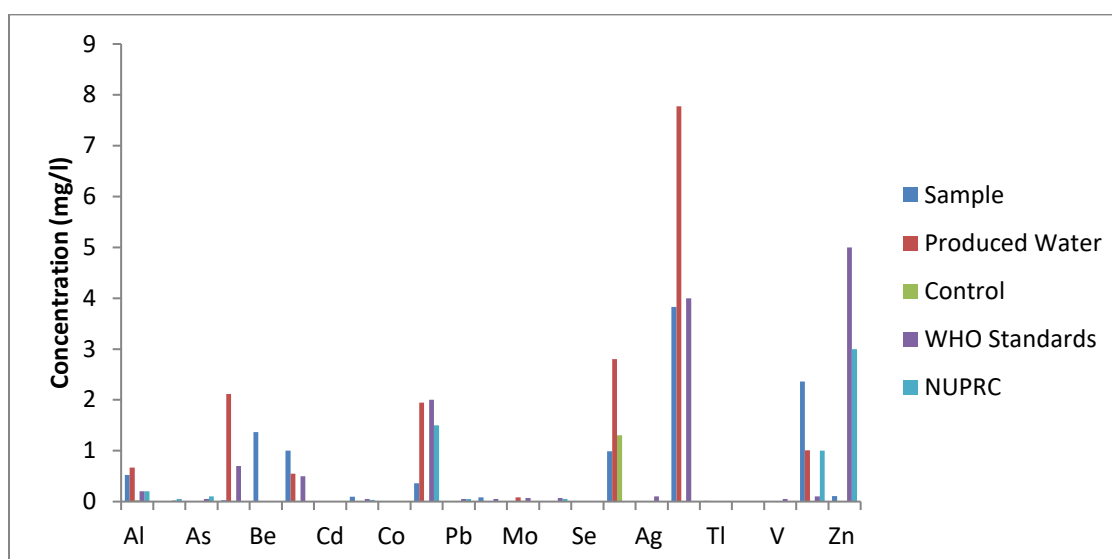
#### 3.1 Heavy Metals

The analysis of drilling fluid effluent (produced water) and sampled water from the study area, as

well as a controlled sample, revealed significant variations in the concentrations of investigated heavy metals. While some heavy metal concentrations fell within the recommended limits set by the World Health Organization (WHO), Nigerian Upstream Petroleum Regulatory Commission (NUPRC), and Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN), others exceeded these international standards.

**Table 2:** Concentration of Heavy Metal in Produced Water, Control sample (CTL), WHO, EGASPIN standards and correlation coefficient (R)

Element	L1	L2	L3	L4	L5	Mean L <sub>1</sub> -L <sub>5</sub>	Produced H <sub>2</sub> O	CTL	WHO	EGASPIN	R
Al	0.639	0.252	0.460	0.517	0.741	0.522 ± 0.174	0.6716	0.0262	0.2	0.2	0.781
Sb	ND	ND	ND	ND	ND	-	ND	ND	0.02	0.05	0
As	ND	ND	ND	ND	ND	-	ND	ND	0.05	0.1	0
Ba	0.028	0.025	ND	0.032	0.030	0.029 ± 0.012	2.1138	ND	0.7		0.743
Be	ND	ND	ND	1.365	ND	1.365 ± 0	ND	ND	0.001		0
B	1.293	1.041	1.381	0.024	1.281	1.004 ± 0.428	0.5475	ND	0.5		0.823
Cd	ND	ND	ND	ND	ND	-	ND	ND	0.003		0
Cr	0.030	0.043	0.276	0.026	ND	0.094 ± 0.126	ND	ND	0.05	0.03	0
Co	0.007	0.009	ND	ND	ND	0.008 ± 0.020	ND	ND	0.01		0
Cu	0.318	0.280	0.564	0.336	0.308	0.361 ± 0.076	1.9487	0.0071	2.0	1.5	0.955
Pb	ND	ND	ND	ND	ND	-	ND	ND	0.01-0.05	0.05	0
Mn	0.093	0.060	0.122	0.071	0.080	0.085 ± 0.033	ND	ND	0.05	NA	0
Mo	ND	ND	ND	ND	ND	-	0.0853	0.0126	0.07		0
Ni	ND	ND	ND	ND	ND	-	ND	ND	0.07	0.05	0
Se	ND	ND	ND	ND	ND	-	ND	ND	0.01		0
Si	0.958	0.986	ND	0.850	1.173	0.992 ± 0.123	2.8000	1.3068	NA		0.983
Ag	ND	ND	ND	ND	ND	-	ND	ND	0.1		-
Sr	3.815	3.096	4.257	4.142	3.840	3.830 ± 0.386	7.7767	ND	4.0		0.996
Tl	0.010	ND	ND	ND	0.021	0.016 ± 0.011	ND		0.002		0
Ti	ND	ND	ND	ND	ND	-	ND	ND	NA	NA	0
V	ND	ND	ND	ND	ND	-	ND	ND	0.05		0
Fe	2.056	2.982	0.980	4.435	1.344	2.359 ± 1.343	1.0091		0.1	1.0	0.911
Zn	ND	0.128	0.048	0.161	0.086	0.106 ± 0.079	ND		5.0	3.0	0



**Figure 1:** Concentration of heavy metals in control samples, produced water, and comparison with WHO and NUPRC standards

Notably, the analysis revealed alarmingly high levels of various heavy metals in river and ocean samples, surpassing the recommended limits. The mean concentrations of heavy metals in pentaplicate water samples from the study area, including produced water, control samples, and comparative standards from WHO, NUPRC, and EGASPIN, are presented in Table 2 and Figure 1. The results for individual elements are discussed in detail below.

#### **Aluminum (Al) Concentration and Toxicity**

The mean concentration of aluminum (Al) in the investigated water samples was  $0.522 \pm 0.174$  mg/L, exceeding the control value (0.0262 mg/L) and the World Health Organization (WHO) and Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN) standards of 0.2 mg/L.

A strong positive correlation ( $r = 0.6716$ ) was observed between the Al concentration in the produced water and the Al concentration in the water samples. This correlation suggests that the Al concentration in the produced water significantly influences the Al levels in the surrounding water samples. The correlation study reveals that the concentration of aluminum (Al) in

produced water can significantly increase the levels into surrounding water bodies. This increase raises concerns about potential bioaccumulation, because it results in toxic reactions throughout the food chain, affecting populations of aquatic life and humans who rely on the water for domestic and agricultural purposes (Udo *et al.*, 2017).

Aluminum toxicity poses a significant threat to aquatic life, including fish and other aquatic organisms, even at low concentrations. It can accumulate on the gills of fish, leading to respiratory dysfunction and potential death (EPA, 2021). Additionally, Al toxicity can indirectly affect aquatic insect populations if their predators, such as fish, are susceptible to Al toxicity. Aquatic invertebrates tend to accumulate Al on ion regulatory surfaces, but do not biomagnify it (Gensemer & Playle, 1999). Increased Al concentrations in water bodies can be critical for fish (Teien *et al.*, 2005), and exposure to Al can cause damage to parenchymatous tissues (kidney, liver, spleen) of fish.

Notably, a significant portion of the study area's inhabitants rely on fishing as their primary occupation and source of economic livelihood,



highlighting the importance of addressing Al contamination in the region

**Barium (Ba):** The mean concentration of Ba in the investigated water samples was  $0.029 \pm 0.012$  mg/l and was within the WHO standard of 0.7 mg/L. Ba was not detected in the control sample (Table 1.4). The correlation between the mean concentration of Ba in the water sample and produced water indicated a strong positive correlative coefficient  $r = 0.743$ . This also imply that the concentration of Ba in produced water from petroleum drilling activities in the study area may intensely affect the concentration of Ba in the investigated water samples of Eastern Obolo.  $\text{BaSO}_4$  is a major constituent in the composition of drilling fluid used in drilling processes, and produced water can become contaminated by Barium. Heavy contamination of water body is a grave environmental threat because it affects plants, animals, and humans (Gu *et al.*, 2018; Wang *et al.* 2020; Etesin *et al.*, 2023). Barium can be toxic to aquatic life, particularly fish and invertebrates. Exposure to high levels of barium can cause respiratory distress, reduced growth rates, and increased mortality in fish. Barium can also accumulate in aquatic organisms, potentially biomagnifying up the food chain Human Health. Human exposure to high levels of barium can cause a range of health problems. Barium can affect the cardiovascular system, causing hypertension, cardiac arrhythmias, and cardiac arrest. Exposure to barium can also cause gastrointestinal problems, including nausea, vomiting, and abdominal pain. Additionally, long-term exposure to barium has been linked to an increased risk of cancer (Golding, 2018). A study investigating the produced water from the Mobil QIT effluent point source found evidence of toxicity to aquatic organisms, with significant adverse effects observed in the freshwater fish species *Oreochromis niloticus* (Oluseyi *et al.*, 2020).

### **Beryllium (Be) Concentration:**

Beryllium (Be) was detected in only one study location, with a concentration of 1.365 mg/L (Table 2). Notably, Be was absent in both the control water sample and the produced water. However, the detected concentration exceeded the World Health Organization's (WHO) recommended threshold limit of 0.001 mg/L.

As a known carcinogen and toxic substance (IARC, 2018), beryllium poses significant health risks. The estimated health-based value for Be in drinking water is 12  $\mu\text{g/L}$  (WHO, 2009). Prolonged exposure can lead to intestinal lesions, skin and lung tissue damage, and skeletal system harm (Shiv *et al.*, 2023).

In aquatic environments, high concentrations of beryllium can be fatal to organisms, while low concentrations can cause long-term growth reduction, reproductive issues, and survival problems in microorganisms. Beryllium accumulation in aquatic organisms can enter the food chain, potentially causing oxidative stress, DNA damage, cellular dysfunction, and immune system depression. Chronic beryllium disease symptoms include shortness of breath, unexplained coughing, fatigue, weight loss, fever, and night sweats (US Department of Labor, 2010). Heavy metals have been extensively used as indicators of pollution by numerous scientists, due to their potential to cause harm to both human and aquatic life at elevated concentrations.

**Boron (B):** Boron was detected at varying concentrations in all the study locations with mean concentration of  $1.004 \pm 0.428$  mg/L. Boron was not detected in the control sample but 0.5475 mg/L of Boron was detected in the produced water sample. The correlation between Boron concentrations in produced water to the water sample showed a very positive correlation coefficient of (0.823). This implies that discharge of produced water effluent by oil companies'

operations in Eastern Obolo water bodies is one of the sources of boron contamination in the water of the study area.

**Chromium (Cr):** Cr was detected at varying concentrations in four (4) of the study locations with mean concentration of  $0.094 \pm 0.126$  mg/L. However, Chromium was not detected in the produced water and control water samples. The mean concentration of Cr  $0.094 \pm 0.126$  was higher than 0.05 and 0.03 permissible level required by WHO and EGASPIN. Chromium can bio-accumulate in aquatic organisms and potentially enters the food chain. Cr is highly soluble in water and soil, Cr (VI) is regarded as a hazardous ion that contaminates groundwater and can be transferred through the food chain (Joutey *et al.*, 2015; Kumar *et al.*, 2019a; Kumar *et al.* 2019b and Sharma *et al.*, 2020). Weathering of Cr containing rocks and leaching of soils discharge significant Cr concentrations of chromium into aquatic environment. According a similar research, concentration of Cr in freshwater and seawater range from  $0.1$  to  $117 \mu\text{g L}^{-1}$  and  $0.5$  to  $50 \mu\text{g L}^{-1}$  respectively (Ertani *et al.*, 2017; Sharma *et al.*, 2020). Hexavalent chromium (Cr (VI)) is a known carcinogen, posing a risk to aquatic life and humans consuming contaminated water or organisms, Chromium can affect reproduction, development, and larval survival in aquatic species, including oxidative stress, DNA damage, and disruption of cellular functions. Moreover, Chromium can alter the balance of aquatic ecosystems, leading to changes in species composition and reduced biodiversity. High levels of Chromium can disrupt enzyme functions, nutrient cycling, and other biochemical processes in aquatic organisms. Hexavalent chromium [Cr (VI)] is a global environmental pollutant that increases the risk for several types of cancers and is increasingly being recognized as a neurotoxicant (Sharma *et al.*, 2022; Wise *et al.*, 2022; Vendruscolo *et al.*, 2017). Exposure of

animals to Cr (VI) in drinking water induced tumors in the alimentary tract, with linear and supralinear responses in the mouse small intestine (Zhitkovich, 2011). These and many more make the present of chromium in water a major public health issue. The evaluation of the concentrations of this element in produced water is of environmental significance from pollution viewpoint, especially Ferrochrome Lignosulphate (Chromium pollution) and lead compounds (Lead pollution), (Awaka-ama *et al.*, 2024; Udosen *et al.*, 2010). Determining the sources of chromium contamination in water bodies of Eastern Obolo is crucial in safe guarding the human, plants and animal health in the study area from the potential hazard of the element.

**Cobalt (Co):** Cobalt was detected in location 1 and 2 in the study area with concentrations of  $0.007\text{mg/L}$  and  $0.009 \text{ mg/L}$  respectively. Mean concentration was  $0.008 \pm 0.020$  mg/L. Cobalt was not detected in the produce water and control water sample Table 1. The Concentration and the mean values did not exceed the WHO recommended standard of  $0.01 \text{ mg/L}$ . Cobalt (Co) is an essential nutrient (Andrew *et al.*, 2022), but excessive exposure can cause health effects, including cardiovascular disease, neurological damage, such as hand tremors, muscle weakness, and nerve damage. Cobalt can interfere with thyroid function, leading to hypothyroidism or hyperthyroidism. Inhaling cobalt dust or fumes can cause respiratory problems, including asthma and lung disease. At a certain concentration, cobalt can cause Skin and eye irritation. High levels of cobalt can affect fertility, fetal development, and child growth (Zhang *et al.*, 2020). Prolonged exposure to high levels of cobalt can damage kidney function. Also, cobalt can weaken the immune system, resulting in susceptibility to infections (Tsui *et al.*, 2020). Major sources of cobalt into aquatic environments include its release from mining, smelting, and



refining operations, as well as from the production of cobalt-containing alloys and chemicals (Kummerer *et al.*, 2020). Also, fertilizers and pesticides containing cobalt can enter waterways through soil erosion and runoff (Liu *et al.*, 2019). Inadequate treatment of waste-water such as produced water can lead to cobalt release into aquatic environments (Wang *et al.*, 2020). Cobalt can be released from mining and drilling operations, including those related to oil and gas extraction (Kribek *et al.*, 2019). Regular monitoring of this metal in soil, water bodies and in fact food items necessary to prevent accumulation and adverse effects.

**Copper (Cu):** Copper was detected in all the study locations at varying concentrations. The mean concentration of Cu in the study was  $0.361 \pm 0.076$  mg/L. This level was significantly below the maximum permissible limit recommended by WHO (2.0mg/l) and NUPRC (1.5mg/l), but higher than the control 0.0071 mg/L. Comparing the concentrations of Cu in the investigated water sample ( $0.361 \pm 0.076$ ), control (0.007 Mg/L), produced water (1.949 mg/L) correlation coefficient (0.955), the strong positive  $r$  indicates that the concentration of Cu in the investigated water sample is a direct influence by the concentration in the produce water. Drilling, extraction, and transportation of petroleum products can release copper-containing drilling fluids, pipeline corrosion products, and spillage into waterways (Osuji & Avwiri, 2005). However, Copper-based pesticides and fertilizers used in farming can enter water bodies through runoff (Ekeanyanwu & Nwadinigwe, 2017).

Copper is an essential trace metal necessary for growth and metabolism of all living organisms (Nordberg *et al.* 2007; Woody and O'Neal 2012). Conversely, at higher concentrations, Cu is toxic to humans and animals, Cu is one of the most toxic elements to marine species. At levels just above the permissible limit for growth and reproduction

it can accumulate and cause irreversible harm to some species (Tierney *et al.*, 2010; Woody & O'Neal, 2012). Cu can be toxic to fish, crustaceans, and other aquatic organisms, causing mortality, reduced growth, and reproductive issues (Osuji *et al.*, 2005). Cu can accumulate in aquatic organisms and biomagnify through the food chain, posing risks to humans consuming contaminated seafood (Akpoveta, 2017), and can alter the composition of aquatic communities, favoring tolerant species over sensitive ones (Ekeanyanwu & Nwadinigwe, 2017). It can also affect nutrient availability and cycling in aquatic ecosystems, impacting primary production and ecosystem functioning (Orji, 2018). Chronic Cu exposure can lead to reduced biodiversity and ecosystem resilience in Niger Delta aquatic environments (Ejeh & Nwosu, 2018). It is reported that Consumption of Cu-contaminated fish and shellfish can pose health risks to humans, including liver and kidney damage, as well as increased cancer risk (Osuji & Avwiri, 2005). Unabated contamination can extensively affect fisheries aquaculture, and marine lives leading to blue economic losses and food security concerns (Akpoveta, 2017), especially in the Niger Delta region.

**Manganese (Mn):** Manganese was detected in all samples of the study locations with mean concentration of  $0.085 \pm 0.033$  mg/L. This was slightly higher than the 0.05 mg/L recommended by WHO. The result indicated that Mn was not detected in the produced water and control samples. Manganese is a naturally occurring element and found in surface waters and biota.

Aquatic organisms have exhibited toxic responses to manganese in surface waters (Reimer, 1999). Mn can enter aquatic environment via industrial processes such as steel production, mining, and smelting (Akpoveta, 2020). Drilling activities and extraction of petroleum products can release Mn-containing drilling fluids and pipe corrosion

products into waterways (Osuji & Avwiri, 2020), as well as through Mn-based pesticides and fertilizers used in farming. (Ekeanyanwu & Nwadinigwe, 2020). However, Mn can occur naturally in soil and rocks, leading to background levels in water bodies (Ejeh & Nwosu, 2020).

The disposal of oil and gas drilling fluids, produced water and cuttings pollute both the terrestrial and aquatic environments. It is suspected that there are trace amounts of pollutants in these waste products, which when

bio-accumulated or bio-concentrated, would be detrimental to organisms exposed to them.

The World Health Organization (WHO) has established guidelines for the permissible limits of heavy metals in produced water (WHO 2011). Also, The EGASPIN 2022 permissible standard for heavy metals in produced water is not explicitly stated. However, the NUPRC standard for Produced Water Discharge should be followed strictly.

**Table 3:** Showing the Concentration of Polycyclic Aromatic Hydrocarbons (PAHs) in the study samples

S/N	Compounds	Concentration of Polycyclic aromatic hydrocarbons in ppm						Produced H <sub>2</sub> O	Ctl
		L1	L2	L3	L4	L5	mean(L1-L5)		
1	Naphthalene	3.810	3.810	3.810	3.810	3.810	3.810	206.510	9.203
2	Acenaphthylene	0.312	-0.376	7.241	1.665	19.055	5.579	276.267	1.030
3	Acenaphthene	-0.184	-0.208	7.481	0.863	14.774	4.545	90.630	0.536
4	Fluorene	0.151	0.222	9.482	2.405	7.511	3.954	28.545	2.561
5	Ph66enanthrene	0.804	1.920	5.817	15.400	3.479	5.484	12.213	12.771
6	Anthracene	0.259	0.314	2.267	17.687	0.977	4.301	14.135	1.289
7	Fluoranthene	1.005	0.385	1.190	5.970	1.085	1.927	5.827	2.921
8	Pyrene	1.091	0.312	1.054	4.895	1.098	1.690	19.021	2.296
9	Benz(a)anthracene	0.456	0.033	0.976	0.723	0.400	0.518	18.827	0.538
10	Chrysene	0.390	0.215	0.890	0.959	0.482	0.587	8.200	0.741
11	Benzo(j)fluoranthene	0.161	-0.039	1.742	2.744	-0.029	0.916	24.310	0.714
12	Benzo(k)fluoranthene	-0.354	-0.039	1.742	2.744	-0.029	0.813	24.310	0.714
13	Benz(a)pyrene	0.241	0.024	0.984	0.166	0.095	0.302	7.346	0.160
14	Indeno(1,2,3-cd) pyrene	0.919	1.004	1.806	1.348	3.526	1.720	10.151	0.648
15	Dibenz(a,h)anthracene	0.542	1.383	7.922	1.269	1.426	2.508	34.889	0.514
16	Benzo(g,h,i)perylene	0.881	0.505	1.262	1.535	0.633	0.963	7.495	0.613

### Benzo(j)fluoranthene

The result of the concentration of PAHs is given in Table 3. The concentration of Benzo(j)fluoranthene in produced water (24.310 ppm) was significantly higher than the control sample (0.714 ppm). Considering Produced water and European Union (EU) standards, the concentration of Benzo(j)fluoranthene in

produced water (24.310ppm) exceeded the European Union standard (0.00001 ppm) by a factor of approximately 2,430,000. The mean difference (0.916 ppm) is lower than the concentration of Benzo(k)fluoranthene in produced water (24.310 ppm) but higher than the control sample (0.714 ppm). The concentration in the produced water sample exceeded the EU

standard by an extremely large margin. The mean difference was relatively small compared to the concentration in produced water while the control sample indicated a relatively low concentration of Benzo(j)fluoranthene.

### **Benzo(a)pyrene (BaP)**

Benzo(a)pyrene (BaP) is a Polycyclic Aromatic Hydrocarbon (PAHs) known for its carcinogenic properties (IARC, 2010). Comparing the mean difference of Benzo(a)pyrene (BaP) concentrations in the control and Produced Water samples, and evaluating them against the European Union (EU) standard, indicates that the concentration of Benzo(a)pyrene (BaP) in Produced Water (7.346 ppm) was significantly higher than the control sample (0.160 ppm). The concentration of Benzo(a)pyrene (BaP) in Produced Water (7.346 ppm) exceeded the European Union standard (0.00001 ppm) by a factor of approximately 734,600. The mean difference (0.302 ppm) showed a lower concentration compared with the concentration of BaP in Produced Water (7.346 ppm). However, it was higher than the control sample (0.160 ppm).

From the results, the Produced Water sample exceeded the EU standard by an extremely large margin, indicating potential environmental and health risks. The mean difference was relatively small compared to the concentration in Produced Water, suggesting a significant difference between the control and Produced Water samples. A relatively low concentration of Benzo(a)pyrene (BaP) was obtained in the control sample, indicating a possible baseline level for comparison.

### **Indeno(1,2,3-cd) pyrene (IcdP)**

Indeno(1,2,3-cd) pyrene (IcdP) is a Polycyclic Aromatic Hydrocarbon (PAHs) known for its carcinogenic and mutagenic properties (IARC, 2010). The concentration of Indeno(1,2,3-cd) pyrene (IcdP) obtained in Produced Water (10.151

ppm) was similarly significantly higher than the control sample (0.648 ppm). The concentration of Indeno(1,2,3-cd) pyrene (IcdP) in Produced Water (10.151 ppm) exceeded the European Union standard (0.00001 ppm) by a large factor of approximately 1,015,100. The result indicated that the mean difference (1.720 ppm) was lower than the concentration of Indeno(1,2,3-cd) pyrene (IcdP) in Produced Water (10.151 ppm) but the value obtained for the control sample (0.648 ppm) was higher. The Produced Water sample exceeded the EU standard by a large degree of margin, indicating potential environmental and health risks. The mean difference was relatively small compared to the concentration in Produced Water, suggesting a significant difference between the control and Produced Water samples with the control sample showing a relatively low concentration of Indeno (1,2,3-cd) pyrene. These results indicate possible baseline level for comparison.

Polycyclic Aromatic Hydrocarbons (PAHs) can be released into the environment during crude oil drilling operations, including the use of drilling fluid, accidental spills and produced water disposal and management. Polycyclic Aromatic Hydrocarbons (PAHs) can have significant impacts on the eco-system of the area of industrial operations. Some of these effects include water pollution, soil contamination, toxicity to aquatic life, bio-accumulation into tissues of organisms, air pollution, carcinogenic effects and the disruption of the ecosystem leading to extensive impacts on human health (Awaka-ama *et al.*, 2024).

The significantly high concentration levels of some PAHs in the study area are of environmental concern in order to abate the level of environmental pollution in the Niger Delta Region.

### 3.2 Bioaccumulation and toxicity

The accumulation of heavy metals and PAHs in aquatic organisms can have detrimental effects on human health, particularly for those consuming contaminated seafood. Further research is needed to investigate the bioaccumulation and toxicity of these pollutants in the food chain as the result suggest a positive correlation between drilling intensity and pollution levels, highlighting the need for more stringent regulations and environment monitoring.

### 3.3 Correlation with drilling activities

A significant positive correlation was observed between drilling intensity and pollution levels, underscoring the critical role of drilling activities in contributing to environmental degradation in the Niger Delta region.

### 3.4 Options Available for Managing Produced Water

In Produced Water management, some of the available current options to the oil and gas operators include;

- (i) Prevention of the production of water unto surface facility using separators and down-hole which separate water from gas and oil stream, and re-inject it into suitable formation
- (ii) Injection of produced water which involves re-injection of produced water into the same formation or other suitable formations. This process includes the conveyance of the Produced Water from the production to injection site and proper purification of the Produced Water before injection in order to reduce fouling and scaling agents and possible bacteria growth.
- (iii) Produced Water Discharge involving the treatment of Produced Water to meet Onshore or Offshore discharge regulations. Although some locations or regions do not require treatment before discharge.

- (iv) Reuse of waste water for oilfield operations involving the treatment of produced water to meet required quality for drilling operations.

### 4.1 Conclusions

The Niger Delta oilfields' drilling activities pose significant environmental and health risks due to elevated levels of certain heavy metals and Polycyclic Aromatic Hydrocarbons (PAHs) in drilling fluids and nearby water bodies. Notably, some of these pollutants surpass international standards, imperilling aquatic life, contaminating soil and groundwater, and jeopardizing human health. Furthermore, statistical analysis revealed a strong positive correlation between produced water and heavy metal concentrations in the aquatic ecosystem, suggesting that produced water is a primary source of heavy metal pollution in the study area.

- (a) Environmental pollution: The discharge of drilling fluids and effluents contaminated with heavy metals poses a significant threat to aquatic life and human health in the Niger Delta region.
- (b) Human health risks: Exposure to these heavy metals can lead to severe health problems, including cancer, neurological damage, and reproductive issues.
- (c) Regulatory framework: The study highlights the need for stricter regulations and enforcement to prevent environmental degradation and protect public health and the ecosystem.

This study underscores the urgent need for environmental stewardship and responsible management of drilling fluids and effluents in the Niger Delta oilfields. By adopting sustainable practices and enforcing regulations, we can mitigate environmental pollution, protect human health, and ensure a safer environment for future generations. By assessing the environmental and health impacts of Produced Water and drilling fluids effluents, this study contributes to develop data on crude oil drilling operations and promotes the development of sustainable practices in the

responsible management of oil and gas operations in the Niger Delta region.

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