**POLYCLIC AROMATIC HYDROCARBONS (PAH’s) CONCENTRATIONS IN OILFIELD PRODUCED WATER FROM PETROLEUM IMPACTED NIGER DELTA ENVIRONMENT**

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# Abstract

The Niger Delta region, located in Southern Nigeria, is a significant hub for oil and gas production, fostering economic growth and energy security in West Africa sub-region. Drilling activities in this region generate substantial amounts of Produced Water - a large waste stream that develops in oil and gas exploration and production, where water is brought up from the reservoir together with the oil/gas. These pose significant environmental and health risks. Beyond ancillary components, Polycyclic Aromatic Hydrocarbons (PAHs) which are a group of organic compounds with two or more fused aromatic rings, are the main constituents in Produced Water that constitute critical environmental concern. This study investigates the concentrations of PAHs in Produced Water from a Petroleum impacted Niger Delta environment, compared with samples from an un-impacted location to assess their potential risk to the environment. Fourteen (14) samples of Produced Water were collected from seven (7) different oil drilling locations and analyzed for PAHs specifically classified as “priority pollutants” by the US-EPA,using Gas Chromatography - Mass Spectroscopy (GC-MS). The results obtained from the environmental media revealed elevated levels of some carcinogenic PAHs viz: Benzo(a)pyrene (7.346 ppm), benzo(b)fluoranthene (24.310 ppm), benzo(k)fluoranthene (24.310 ppm), benzo(g,h,i)perylene (7.495 ppm), and indeno(1,2,3-cd)pyrene (10.151 ppm), significantly exceeding acceptable threshold limits of international standards. In contrast, the control samples showed comparatively lower concentrations.The results obtained for the control samples ranged between 0.160 ppm [being the lowest for Benzo(a)pyrene] - 12.771 ppm [being the lowest for Phenanthrene].The results revealed a strong positive correlation between Produced Water and PAH concentrations in the aquatic ecosystem. By assessing the pollution burden and the environmental and health impacts of Produced Water, this study contributes to develop valuable data on the impact of crude oil drilling operations, underscoring the need to mitigate environmental risk and the imperative for sustainable management of Produced Water effluent in the Niger Delta oilfields.

***Keywords:*** *Produced Water, Polycyclic Aromatic Hydrocarbons, Environment, Pollution, Niger Delta.*

**1.0 Introduction**

Renewable and alternative energy sources have increasingly garnered industry-wide attention, contributing to a more diversified energy mix towards transformation to a low carbon economy and a sustainable energy future. This is due in part, to increasing global prosperity which drives growth in energy demand, as oil and gas production volumes reflect the overall economic trend. However, considering the current global energy mix and indeed outlook, oil and gas production continues to provide a comparatively huge and reliable energy source that drives global economy. Worldwide, new oilfield development projects evidently continue to dot the oil and gas energy landscape.

Drilling operations are generally classified into offshore and onshore drilling. Some environmental challenges have been associated with drilling operations including a variety of wastes such as drill cuttings, spent drilling fluid and Produced Water. Produced Water is a large waste stream that develops in oil and gas exploration and production, where water is brought up from the reservoir together with the oil/gas. This water is a mixture of formation water, injection water, and small volumes of condensed water from gas production and aqueous residues of treatment chemicals. The influent waters, and production chemicals sometimes are injected into a reservoir to enhance both recovery rates and the safety of operations and these surface waters and chemicals sometimes penetrate to the production zone and are recovered with oil and gas during production (Neff, 2002).

Produced Water equally constitute the largest waste stream by volume in oil and gas production operations on several offshore platforms (Clark and Veil, 2009; Stephenson, 1992; Kraus, 1995), and may account for 80% of the wastes and residuals produced from natural gas production operations (McCormark *et al.,* 2001). It is reported that currently, the global output of Produced Water exceeds oil production at a volumetric ratio of estimated 2:4, which interestingly is a little less than the data reported in 2009 with a ratio of 3:1 at the time and 10:1 in the United States (Clark and Veil, 2009), with a total oil production worldwide of 95.2 million barrels in 2019. A recent report has shown that Produced Water production has reached 250 million barrels per day (Haneef *et al,* 2020a), and of great concern, 40% of which is discharged untreated into the environment (Haneef *et al.,* 2020b). At the current scale of oil and gas production and with the maturation of oil fields, it is expected that the ratio of produced water/extracted oil will lead to a further corresponding increment (IEA, 2024; McCabe, 2012). Another perspective is that one of the world’s largest oil reserves, containing over 169 billion remaining barrels of recoverable bitumen, located in Athabasca oil sands deposit - Alberta, Canada, undergoes extraction process resulting in raw tailings at a 9:1 volume ratio to extracted oil (Alberta Chamber of Commerce, 2004). Hence, the future of oil sand exploration will also have implications on the amount and the nature of Produced Water in the near future. In the Middle East oilfields, concerns have been raised about the impact of Produced Water and the currently implemented techniques for its management and disposal (Salem and Thiemamn, 2022).

In the course of oil and gas production in Nigeria, about one billion barrels of Produced Water is discharged per year (Isehunwa and Onovae, 2011). Since the discovery of oil in the Niger Delta region in 1956, the producers have focused primarily on maintaining high profitability by reducing operational costs and unnecessary capital expenditure to the minimum and these operational strategies include Produced Water management and disposal as one of the cost reduction plans (Ewim *et al.*, 2023), resulting in giving little attention to their environmental risks. It is reported that 7500 -11,500 tonnes hydrocarbon is released to the environment yearly as a result of produced water discharges worldwide (Salem and Thiemamn, 2022; Holdway, 2002). Considering the large volume of estimated hydrocarbon released worldwide to the environment as a result of Produced water discharges, this can potentially alter the natural state of the environment which may lead to various adverse environmental impacts. This highlights a global concern about the impacts of large volumes of drilling wastes, particularly when they are improperly released into the environment (Awaka-ama *et al.,* 2025). The quantity and quality of Produced Water highly depend on where, when and how hydrocarbons are produced, as a function of geological formations. This leads to differences between Produced Water samples and a high variability from one sampling site to another. For instance, salinity (salt concentration) described as the index of amount of dissolved solids (TDS) in water (Nsi *et al.,* 2020), can vary in conventional oil and gas well produced waters from 1000 - 400,000 mg/L (Bird *et al*., 2002), as well as elemental ion contents. Raji and Abejide (2013) reported that the exploration and production of oil within the Niger Delta Environment has brought changes to their eco-system. With this huge volume of Produced Water generated, and with the attendant issues as highlighted, it is of critical environmental imperative to evaluate and analyze the hydrocarbon burden in produced water samples from the petroleum impacted area. It is important to emphasize that Produced Water management must be in full compliance with the Nigeria Upstream Petroleum Environmental Regulations (2022). Apart from ancillary components, the main constituents in produced water that constitute critical environmental concern, that should be characterized, analyzed and measured is the PAHs content. Since no two Produced Waters are alike, region – specific studies are necessary to investigate the environmental risks associated with its discharge. This research considered it of utmost environmental imperative to investigate in the study area, a group of five (5) PAHs covered under the Water Framework Directive (WFD) (Directive 2000/60/EC) to assess their likely potential risk to the environment. Also, this group of hydrocarbons is listed in Annex I of the related Environmental Quality Standards Directive (EQSD) (2008/105/EC) amended by the Priority Substances Directive (2013/39/EU) and consists of benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene. These compounds are higher molecular weight PAHs comprising 5- and 6-rings, with Benzo(a)pyrene being the most carcinogenic of the group (European Union, 2012). Hence, this has been the main aim and basis that necessitated this research in the study area.

* 1. **Outlook and economic relevance of the Niger Delta**

The Niger Delta region, situated in Southern Nigeria, is the largest wetland in Africa and among the largest globally (Izah and Aigberua, 2023; Nnaemeka, 2020). It spans approximately 70,000 square kilometers with rich and diverse ecosystems, including mangroves, swamps, and tropical rainforests (Nnadi *et al.,* 2022). It has an estimated population of over 30 million people in the region (Figure 1a). The region is endowed with vast natural resources, particularly oil and gas, which account for more than 90% of Nigeria’s export earnings and approximately 80% of government revenue (Kadafa *et al.,* 2012). The region holds immense significance for Nigeria and by extension the Gulf of Guinea, economically, ecologically and in terms of energy security. The economic importance of the region can be attributed primarily to its huge hydrocarbon reserves. Nigeria’s economic growth and development relies strongly on the oil and gas resources of the Niger Delta. These resources constitute over 90% of the country’s export earnings and approximately 80% of its government revenue (Ite *et al.*, 2018; Kadafa *et al.,* 2012).

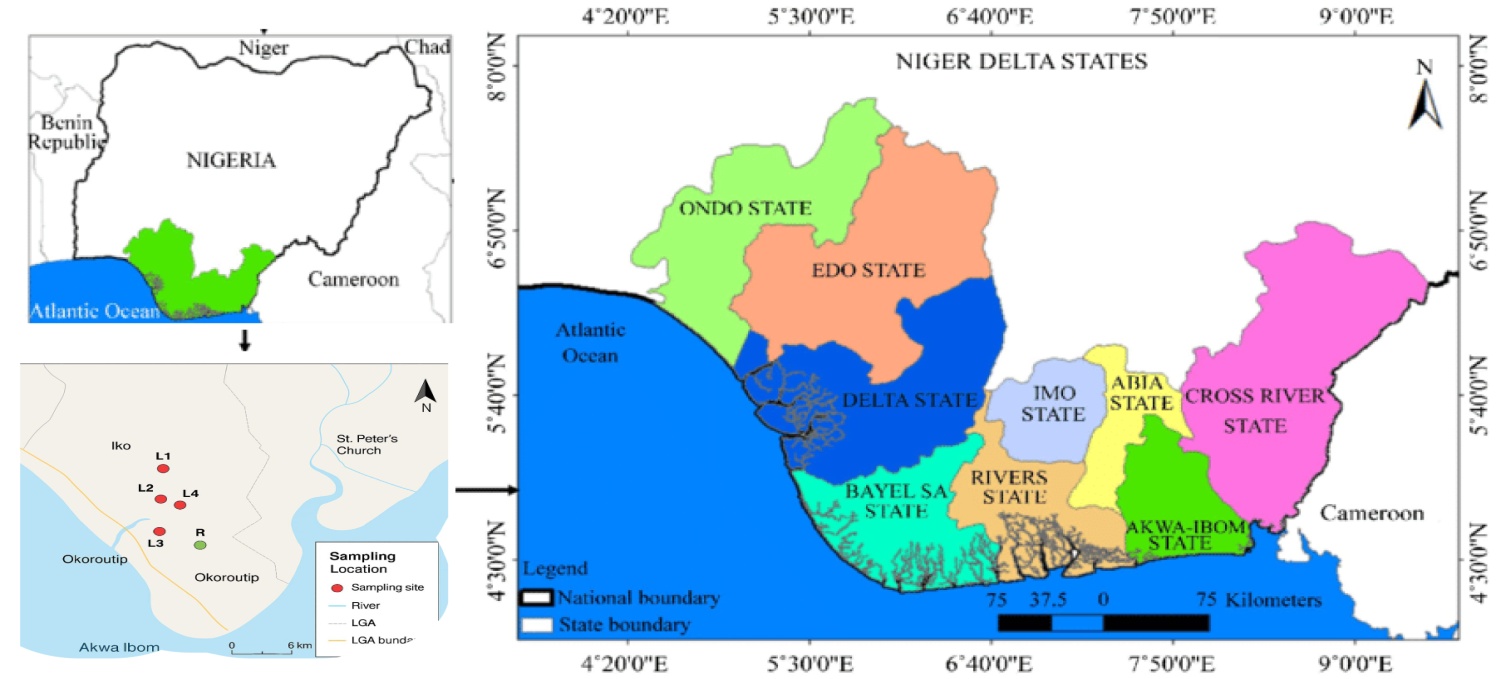


Figure 1a: Maps of Nigeria and the Niger Delta Region*.*

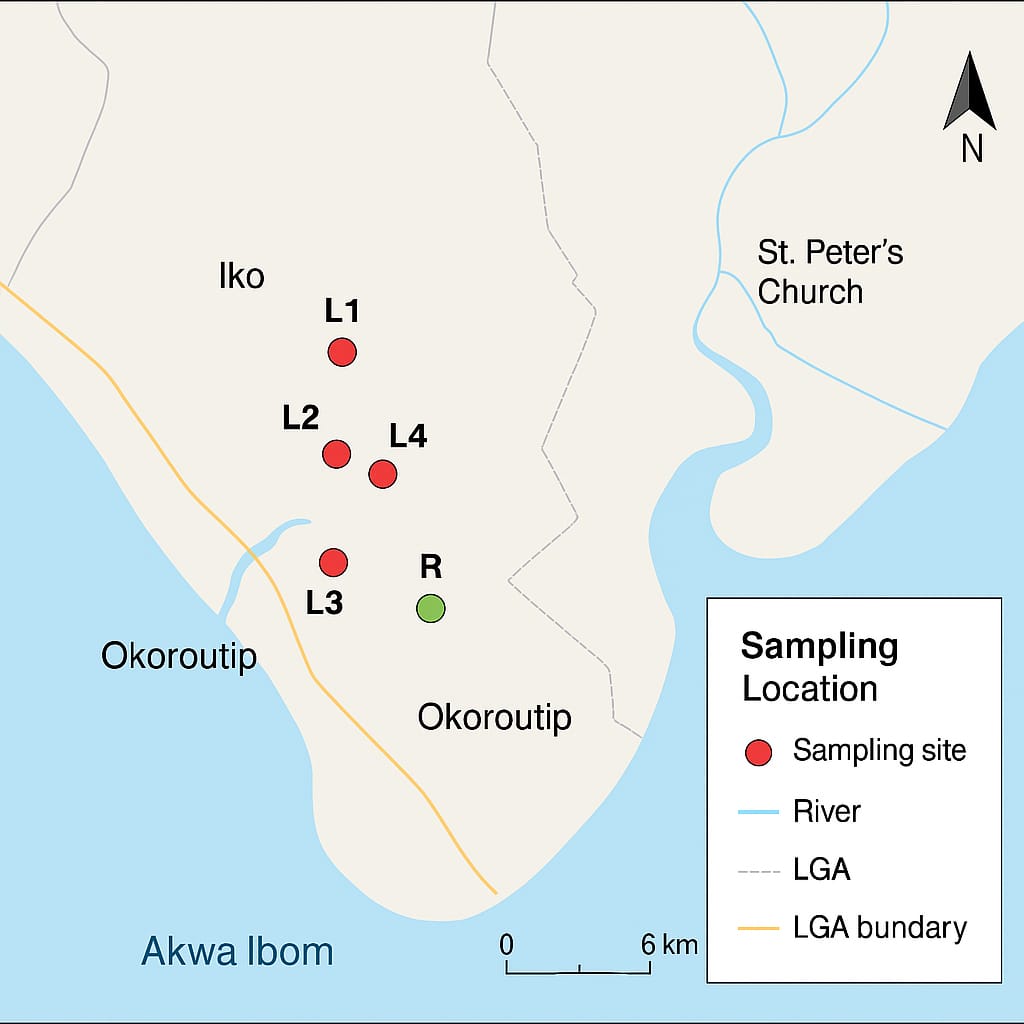


Figure 1b: Map of study area showing sampling points

The oil and gas sector in Nigeria (with proven oil and gas reserves of 36.9 billion barrels and 209.26 trillion cubic feet respectively) contributes approximately 45% of its GDP, indicating that the country’s economic and political stability are intrinsically tied to crude oil, making it crucial to its survival (Ewim *et al.,* 2023). The sector has been a key driver of Nigeria’s economic growth and development, with revenues from the sector providing finance for various infrastructural projects, social services, and other government initiatives (Wilson, 2012). Moreover, it is pertinent to emphasize that the Niger Delta region has recently become the fulcrum of the nation’s drive towards blue-economy and hosts numerous other economic activities, such as agriculture, fisheries, and forestry, which provide livelihoods to a significant portion of the local population. Ecologically, the Niger Delta is a critical area, boasting a diverse ecosystems, including mangroves, swamps, and tropical rainforests. These ecosystems support a high level of biodiversity, including various endangered and endemic species, making the region a global hotspot for conservation (Akani *et al.,* 2022; Elisha and Felix 2021). The wetlands naturally provide essential ecosystem support functions such as flood control, water purification, and carbon sequestration, which have local, regional, and global implications for climate regulation and environmental stability (Clarkson *et al.,* 2013).

Oil and gas production, largely in the Niger Delta region, has played a significant role in Nigeria’s economic development, as the largest oil producer in Africa and ranked 12th globally. Consequently, the region has witnessed plethora of environmental and socio-economic challenges, such as widespread pollution and wastewater issues resulting from oil spills, gas flaring, and various industrial activities (Ite *et al.,* 2018). These legacy environmental challenges have been aggravated by weak regulatory frameworks, inadequate compliance and enforcement, unabated corporate and institutional corruption, inadequate investments in sustainable development, environmental management and pollution control measures. The situation is often aggravated by poorly maintained operational infrastructure and the environmental and thermal oxidation conditions which affect the morphology of the oxides formed by the industrial metals and their alloys (Nyong *et al*., 2022). This may lead to the elevations of the concentrations of heavy metals, PAHs, TPH and THC in the environment, posing a potential risk to the ecosystem and human health (Awaka-ama *et al.,* 2024). Consequently, the region has become the epicenter of a complex nexus of environmental degradation, social inequity, and economic under-development, with far-reaching implications for the future of Nigeria and the well-being of its people ( Ijaiya, 2014).

* 1. **Sources and Chemical Compositions of Produced Water**

Anthropogenic sources of PAHs include industries (e.g., those dedicated to the extraction and exploitation of petroleum derivatives (Patel *et al.,* 2020). Since Produced water is a complex mixture of dissolved and particulate organic and inorganic chemicals, its physical and chemical properties vary widely depending on the geologic age, depth, and geochemistry of the hydrocarbon-bearing formation, as well as the chemical composition of the oil and gas phases in the reservoir. Production chemicals utilized during production also play a critical role. Additionally, the type of hydrocarbon product being produced influence the physical and chemical properties of the Produced Water.

Normally, oil, gas and water exist at equilibrium in hydrocarbon reservoirs; a small proportion of hydrocarbons will dissolve in the water due to their inherent solubility. Therefore, it is inevitable to produce hydrocarbons from the reservoir without producing water, which naturally co-exists in these hydrocarbon reservoirs. Natural water present in oil and gas formations can be a source of produced water (Salem and Thiemamn, 2022). The initial stages of processing involve the separation of water from the hydrocarbon. Operational activities which constitute sources of produced water include Water injection, water flooding or steam flooding and these operations are frequently used to increase oil production from reservoirs. Additionally, water may infiltrate from non-hydrocarbon layers into adjacent hydrocarbon reservoirs, which can then be drawn to the surface as produced water (Al -Ghouti *et al*., 2019). Additionally, a small amount of light aromatic hydrocarbons and suspended oil droplets will be dissolved in the produced water drawn to the surface. Also present are naturally occurring compounds that were dissolved or dispersed from the geologic formations and migration pathways in which the produced water resided for millions of years.

In some hydrocarbon reservoirs where water-flooding and steam flooding is used to increase hydrocarbon production, it is reported that the properties and volume of the produced water may change considerably due to water injection into the hydrocarbon formation (McCormack *et al.,* 2001). Some of the typical Produced water constituents are inorganic salts (expressed as salinity, total dissolved solids (TDS), or electrical conductivity), metals, radioisotopes, oil and grease, a wide variety of organic chemicals: BTEX (benzene, toluene, ethylbenzene, and xylenes), polycyclic aromatic hydrocarbons (PAHs), organic acids, and phenols (Awaka-ama *et al.,* 2025). In addition, chemical additives such as biocides, demulsifiers, scale and corrosion inhibitors from oil fields (Henderson *et al.*, 1999), methanol and diethylene glycol from gas fields can be found that come from the drilling, fracturing, or from operating the well and many additives, laden with toxic properties and used in its composition are not toxic-free and therefore regulated (Awaka-ama *et al.,* 2024; Gazali *et al.,* 2017; Danforth *et al.,* 2020; Teixeira *et al*., 2024). It is reported that that about 53% of chemicals that are used in drilling operation are discharged as wastes and thus cause the pollutants burden in the environment (Marsh, 2003; Salem and Thiemamn, 2022). However, Produced water from oil and gas operations can contain PAHs, such as benzo(k)fluoranthene, due to the presence of these compounds in the source rock and the extraction process.

**Table 1: Sixteen molecules classified as “priority pollutants” by the US-EPA and commonly released in Offshore environment.**







# 2.0 Methodology

**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, Mkpat 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 [ Figure 1b], (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). The control sample was obtained from Itu. Itu LGA is located in the south-south region of Nigeria, covering an area of approximately 606 km². 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.

# Materials and Methods

Produced Water was obtained from a fresh oil well operated by Oil Company ‘X’. 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. Conc. HNO3 was used to prevent the reactivity of other compounds. The samples were analyzed using Gas Chromatography - Mass Spectroscopy (GC-MS).

**Collection of Samples:** Water 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: 4.508093º /7.727900º, sample two (2) was collected at location (L2)-Lat/Lon:4.508093 º/ 7.727900º, sample three (3) was collected at location (L3) -Lat/ Lon:4.508347 º / 7.727900 º, sample four (4) was collected at location (L4)-Lat/ Lon:4.515646º/7.769593º, sample five (5) was collected at location (L5)-Lat/ Lon:4.513401 º / 7.753092º and the control sample (6) was collected at location (R)-Lat/Lon:5.152504º /7.947876 º. Sample storage and preparation of composite samples were done according to standard and best practice.

**Results and Discussion**

The properties and composition of contaminants in produced water vary considerably in different geological formations; therefore, in this study, produced water samples from various oil wells in the study area were analyzed to determine their PAH concentrations, which are critical in determining the environmental and economic risks from its discharge.

**Table 2**: The Concentration of Polycyclic Aromatic Hydrocarbons (PAHs) in the study samples

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **S/N** | **Compounds** | **Concentration of Polycyclic aromatic hydrocarbons in ppm** | | | | | |  |  |
|  |  | **L1** | **L2** | **L3** | **L4** | **L5** | **mean(L1-L5)** | **Produced H2O** | **Control (Ctrl)** |
| 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 | Phenanthrene | 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 |

# The structural formulae of the most common low and high molecular weight PAH’s released in drilling operations is given in Table 1. Two-ringed PAH’s such as naphthalenes and to a lesser degree three-ringed PAH’s such as anthracenes and phenanthrenes are readily soluble in water, making them more available for biological uptake, but also making them more susceptible to degradation. In contrast, four-ringed and five-ringed PAH’s such as benzopyrenes are insoluble in water. However, they tend to biodegrade much more slowly in the aquatic environment than less extended aromatic systems. Benzo(a)pyrene leads to mutagenic metabolites and is categorized as a group 1 carcinogen by the International Agency for Research on Cancer (IARC, 2010). Also, Benzo(g,h,i)perylene is considered to be mutagenic as well as a carcinogen. It readily bio-accumulates in aquatic organisms. PAHs are known for their low affinity to water and their solubility decreases with increase in molecular weight. Hence, the lighter PAHs are mostly found dissolved in the water column while heavier compounds have a high capacity to adsorb on suspended particles as well as on non-polar matrices, which promotes their bioaccumulation in aquatic animals and sediments ( Maletic *et al.*, 2019).

# Benzo(j)fluoranthene (BjFln)

The result of the concentration of PAHs is given in Table 2. The concentration of Benzo(j)fluoranthene in produced water (24.310 ppm) was significantly higher than the control sample (0.714ppm).

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 (0.714ppm). 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. According to IARC, 2010 and Cattley *et al.,* 2023, BjFln are classified as possible carcinogens.

# 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 (Ctrl) 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) indicated a lower concentration compared with the concentration of BaP in Produced Water (7.346ppm). However, it was higher than the control sample (0.160 ppm). In general, the results obtained for the control samples ranged between 0.160 ppm [being the lowest for BaP] - 12.771 ppm [being the lowest for Phenanthrene]. BaP is classified by the International Agency for Research on Cancer (IARC) as a known carcinogenic to humans, being also recognized as a genotoxic, mutagenic, epigenetic, teratogenic, and neuro-toxic substance (Bukowska *et al.,* 2022), Benzo(a)pyrene has been identified as the most carcinogenic of the group (European Union, 2012).

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 (0.648ppm). 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 very large degree of factor of approximately1,015,100. 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), however the value obtained for the control sample (0.648ppm) 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. Indeno(1,2,3-cd) pyrene (IcdP) listed as a priority pollutant, is classified as carcinogenic to humans.

Similarly, the concentration of benzo(k)fluoranthene (24.310 ppm) in Produced Water was higher than the value obtained in the control (0.714 ppm). The European Union (EU) has established standard threshold limits for the concentration of benzo(k)fluoranthene and other polycyclic aromatic hydrocarbons (PAHs) in produced water, particularly concerning its impact on drinking water and the aquatic environment such as the study area of this research. Benzo(k)fluoranthene, a carcinogenic PAH, is regulated under the Drinking Water Directive (EU) 2020/2184, which sets a maximum concentration of 0.0001 ppm for benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, and indeno(1,2,3-cd)pyrene respectively.

Likewise, benzo(a)pyrene, benzo(k)fluoranthene and benzo(g,h,i)perylene have been listed as substances of very high concern (SVHCs) under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) Regulation (EC/1907/2006). Benzo(a)pyrene is listed because of its carcinogenic, mutagenic and reprotoxic (CMR), persistent, bioaccumulative and toxic (PBT), and very persistent and very bioaccumulative (vPvB) properties. Benzo(k)fluoranthene because of its carcinogenic, PBT and vPvB properties, and benzo(g,h,i)perylene because of its PBT and vPvB properties (Environment Agency, 2019). As these PAHs persist in the environment, accumulate in biota and food chains, and have potential adverse effects on aquatic life and humans, they are classed as priority hazardous substances and ubiquitous PBTs (uPBTs) under the EQSD (2008/105/EC amended by 2013/39/EU).

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.

**BTEX and Benzenes**

# The most abundant hydrocarbons in produced water are the one-ring aromatic hydrocarbons, benzene, toluene, ethylbenzene, and xylenes (BTEX) and low molecular weight saturated hydrocarbons. BTEX may be present in untreated produced water from different sources at concentrations as high as 600 mg/L. Produced water also contains small amounts of C3- and C4-benzenes. Benzene usually is most abundant and its concentration decreases with increasing alkylation (Dórea *et al.*, 2007; Neff *et al*., 2011). Because BTEX are extremely volatile, they are lost rapidly during produced water treatment by air stripping and during initial mixing of the produced water plume in the ocean (Gabardo *et al.* 2011). BTEX cause several environmental and harmful human health problems and even at low concentrations are genotoxic, carcinogenic, ototoxic and neurotoxic (Udo *et al.,* 2023).

# Generally, Produced Water discharges from offshore oil and gas platforms are a significant source of polycyclic aromatic hydrocarbons (PAH’s) released to the aquatic environment. PAH content in operational discharges from the offshore industry portends environmental and health concern as many of the PAH’s are equally toxic and lipophilic such that they can be adsorbed by marine organisms, hence concentrates along the food chain. Although PAH’s are classified as persistent organic pollutants (POP’s), these compounds tend to biodegrade in the marine environment, where biodegradation makes them less lipophilic and consequently less likely to accumulate in the marine food web, and similarly non-biodegraded PAH’s tend to concentrate in the sediments of water bodies (Lofthus *et al.,* 2018).

# In terms of toxicity, the accumulation of PAH’s in aquatic organisms can have detrimental effects on human health, particularly when contaminated seafood is consumed. The data from this work also reveal a significant positive correlation between drilling activities and pollution levels, underscoring the critical role of drilling operations in contributing to environmental degradation in the Niger Delta region.

# Produced Water Treatment and Management Options

Due to a myriad of challenges including institutional, environmental, socio-economic, operational and prevailing business climate, majority of oil and gas companies in the Niger Delta region have moved operations into deep offshore. Therefore, Produced Water must be handled with utmost care in compliance with the NUPRC (2022) standards for disposal and handling. Drilling waste can have different potential impacts depending on where it is discharged (Umanah, 2025). The treatment, disposal and management of produced water are critical for sustainable oil and gas production. With the large amount of Produced Water generated in the course of drilling operations, it is of immense importance to manage it, taking into account cost effectiveness and environmental sustainability. Produced water must be treated efficiently to remove all pollutants so it can be reused or otherwise managed. For example, Produced Water that is injected for enhanced oil recovery (EOR) or for disposal should receive different treatments than Produced Water that is discharged. Components such as free oil, solids, and bacteria should be treated and removed from produced water prior to injection. Additionally, chemicals can be used to protect underground formations, preserve equipment and improve treatment processes. However, the case is different for discharging, where produced water that has high contents of oil, grease, salts and toxic chemicals must be treated to remove these components. Treatment technologies that result in reusable effluents and meet economic requirements are preferred for handling all types of effluents.

IPIECA, the global oil and gas industry association for advancing environmental and social performance, which govern decisions regarding the reuse of Produced Water from their operations, had identified the key factors regarding Produced Water management as: economic viability, regulatory (permits, social and corporate policy) and infrastructure (Salem and Thiemann, 2022). From an environmental perspective, circular economy models and the principle of initially deploying technologies to minimize Produced Water volumes and of reusing and recycling Produced Water are paramount. However, if neither of these is readily practicable, disposal becomes the final option (Hedar and Yono, 2018). There are concerns that re-injection technique may lead to induced seismicity, surface water and/or subsurface fresh water aquifer contamination. Nevertheless, it is less costly, therefore it is the most practiced strategy to date, with about 90% of Produced Water being re-injected into the subsurface for disposal or for enhanced oil recovery (EOR) (Guerra *et al*., 2011; Liden, 2018).

# Produced Water from oil and gas exploration may contain different types of contaminants at various concentrations. Hence, various treatment technologies have been proposed to deal with Produced water. Often, up to 80% of the Produced Water is re-injected into the oil well in order to maintain the pressure in the well and to manage large amounts of accumulating Produced Water. The quality requirements of the water used for re-injection depend on the permeability of the oil reservoir; thus, in fractured oil reservoirs, the water can move more freely leading to reduced clogging of the reservoir’s pores. Onshore and offshore operations differ in that offshore operations often have the challenge of space constraints and need to deal with the regulatory fact that in many regions water discharged into the sea after treatment should have no more than 40 ppm non-water soluble hydrocarbon content, with a further reduction proposed in the future (Igunnu and Chen, 2014; Olajire, 2020). The Oslo Paris Convention (OSPAR) stipulates that the maximum discharge be reduced to 30 ppm OIW (oil-in-water) and the overall oil discharges in Produced Water be reduced by 15% from the levels found in 1999 (Igunnu and Chen, 2014). In addition, more attention is given to the more soluble organic compounds found in Produced Water, some of which show appreciable toxicity to the aquatic environment. This may lead to an even higher focus on re-injection of produced water in offshore operations. Regardless, produced water treatment on offshore operations allows for a smaller footprint than onshore operations would do. Therefore, generally offshore and onshore operations often favour different Produced Water purification set-ups (Liu *et al.,* 2021). For onshore operations, these can include physical, chemical and biological methods and often a combination thereof, while for offshore operations biological treatment processes are often impracticable due to their large environmental footprint (Judd *et al.*, 2014). Some of these treatment methods are shown in Table 3.

# Table 3: Produced Water Treatment Methods

|  |  |  |
| --- | --- | --- |
| Produced Water Treatment methods | | |
| Physical | Chemical / Processes | Biological |
| Gravity Separation (as Primary Treatment)Hydrocyclones and Centrifugal Separators (as Primary Treatment)Induced Gas Flotation (IGF, as Secondary Treatment)Adsorption Processes (as Secondary or Tertiary Treatment)Membrane Filtration (as Secondary or Tertiary Treatment)Forward Osmosis (as Secondary Treatment)Reverse Osmosis (as Tertiary Treatment)Electrodialysis (as Secondary Treatment)Membrane Distillation (as Tertiary Treatment) | Coagulation Flocculation (as Secondary Treatment)Advanced Oxidation Processes (AOPs) (as Tertiary Treatment) | Microbial Treatment (as Secondary and Tertiary Treatments)Membrane Bioreactor (MBR) |

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

1. 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
2. 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.
3. 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.
4. Re-use of waste-water for oilfield operations involving the treatment of Produced water to meet required quality for drilling operations.
5. Potential uses of non-re-injected Produced Water for irrigation of non-food crops and of landscape greenery in areas faced with fresh water challenge.
6. Photo-degradation and advanced oxidation processes which is currently receiving a lot of interest from researchers as it provides a spectacular route for the resolution of environmental problems through the detoxification and mineralization of organic pollutants and organic wastes. As a process, it is also gaining prominence due to the low cost for its application, moderate process requirements as well as being residue-free (Nyong *et al.*, 2020).

# 4.1 Conclusions

The Niger Delta oilfields' drilling activities pose significant environmental and health risks due to elevated levels of some Polycyclic Aromatic Hydrocarbons (PAH’s) in Produced Water and nearby water bodies. Notably, some of these pollutants surpass International Standards threshold limits, imperiling aquatic life, contaminating soil and groundwater, and jeopardizing human health. Furthermore, statistical analysis revealed a strong positive correlation between Produced Water and PAH concentrations in the aquatic ecosystem, suggesting that Produced Water is a primary source of PAH pollution in the study area. The critical indices of these assessments include:

1. *Environmental pollution*: The discharge of untreated Produced Water effluent contaminated with PAH’s poses a significant threat to aquatic life and human health in the Niger Delta region.
2. *Human health risks*: Exposure to these identified PAH’s can lead to severe health problems, including cancer, neurological damage, and reproductive issues.
3. *Regulatory framework*: The study highlights the need for stricter legislations and enforcement of relevant regulations to prevent environmental degradation and protect public health and the ecosystem.

The data obtained from these findings underscores the urgent need for environmental stewardship and responsible management of Produced Water effluent in the Niger Delta oilfields. By adopting circular economy model, sustainable practices and enforcing regulations, robust systems can be put in place to mitigate environmental pollution, protect human health, and ensure a safer environment for future generations. By assessing the pollution burden and the environmental and health impacts of Produced Water effluent, this study contributes to develop valuable data on crude oil drilling operations and hence, promotes the development of sustainable practices in the responsible management of oil and gas operations in the Niger Delta region of Nigeria.

It is envisaged that increasing use of sustainable drilling systems and abatement technologies has a promising potential to manage and mitigate risks from the PAH concentrations in Produced Water to the environment as well as robustly investigate and understand any impacts through connected systems such as groundwater. Further research is strongly recommended to investigate the bioaccumulation and toxicity of these pollutants in the food chain as the results from this study suggest a positive correlation between drilling intensity and pollution levels, highlighting the need for more stringent regulations and environmental monitoring and enforcement. .

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