

Heavy metal concentration assessment in produced water from production of oil and gas in an onshore field of South-South Nigeria

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International Journal of Frontiers in Engineering and Technology Research, 2026, 11(01), 028–036

Publication history: Received on 06 June 2026; revised on 15 July 2026; accepted on 17 July 2026

Article DOI: <https://doi.org/10.53294/ijfetr.2026.11.1.0019>

Abstract

The types of hydrocarbons found within the geologic strata and the production practice employed for its recovery can have a significant impact on the heavy metal concentration within the produced water. The concentration and mobility of heavy metals (HMs) are controlled by the flow regime, age of the reservoir, and water-rock equilibrium. Thus, it may be difficult to quantify the amount of heavy metals produced with oil and gas produced at any particular instant. However, the occurrence of high heavy metals content in produced water can be toxic to humans and the environment. In this study, the health hazards and concentrations of HMs in two samples (A and B) of wastewater from oil and gas production facilities were determined by using laboratory measurements and statistical methods. Analysis of the output of laboratory measurement shows that the proportions of heavy metal namely Iron, Copper, Cadmium, Chromium, Lead and Zinc in the produced hydro samples were 0.24, 0, 0, 0.325, 4.76, and 0 for sample A, and 0.432, 0.057, 0, 0, 0, 0.356 for sample B. While the majority of the HMs concentrations contained in the produced water were discovered to have no significant health hazards or threats to human health, the unusually high concentration of Pb in sample A signifies a potential contamination source in the formation and/or production method adopted for hydrocarbon extraction. Therefore, it is important to ensure long-term surveillance and control of HMs concentrations in produced water. HMs concentrations beyond the tolerable limit may harm humans and the environment. Hence, this study suggests continuous and real-time surveillance of HMs concentrations in produced water, while ensuring the implementation of policies and best practices that allow safe water management in the Niger Delta, and sanctions meted when there is non-compliance

Keyword: Heavy Metals; Metal Concentration; Produced Water; Oil And Gas; Health Risk

1. Introduction

The largest byproduct of the extraction of oil and gas in underground reservoirs is produced water, which mostly comprises formation water that is extracted together with hydrocarbons. It comprises a complex system of contaminants, including dissolved salts, heavy metals, chemical additives, and naturally occurring radioactive materials (NORMs) (Faruque et al., 2024; Nyieku et al., 2024). The chemical composition of the water produced in oilfields may vary significantly depending on the geographic location, diversity of the reservoirs, interactions between fluids and rocks, changing modes of production, and occurrence of various hydrocarbon-bearing formations with dissimilar lithologies. Additional variations in composition are due to geochemical reactions with residual lubricants in either drilling fluids or oilfield chemicals used in enhanced oil recovery (EOR), and other improved oil recovery (IOR) and EOR

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methods, such as steam injection and water flooding, which introduce external fluids and contribute to chemical variability (Amakiri et al., 2022; Arouri, 2024; Zhang et al., 2024). Such differences, particularly in the concentration of hazardous materials, continue to pose a persistent problem to environmental surveillance, treatment design, and compliance with regulations.

One of the common types of pollutants that should be measured in the produced water systematically is heavy metals (HMs), which has a high atomic mass and poses a significant health risk and threat to the ecosystem. This is especially important in large oil-producing areas, such as the Niger Delta, where the large onshore and offshore mining operations intersect delicate ecological niches (Onyema et al., 2016). The selection of the particular HMs to be used in the study is predetermined by the fact that they are commonly found in oil production activities; they are toxicologically significant and are included in national and international regulations (Bowers and Smith, 2014; Freije, 2015; Li et al., 2019; Mohammad Ali et al., 2021; Szuster-Janiaczek et al., 2018). Correct methods of analysis are essential to determine specific levels of these in produced water samples (Ibanga et al., 2018; Mishra et al., 2017; Wannahari, 2013).

High concentrations of heavy metals (HMs) in produced water, as well as associated environmental and health risks, have been recorded in different studies conducted in the Niger Delta and other oil-producing regions (Ibanga et al., 2018; Ibekwe, 2023; Maduka and Ephraim-Emmanuel, 2019; Okogbue et al., 2018; Oyeyemi et al., 2024). An example is a study by Erakhrumen (2015) on untreated produced water in a local water plant, which discovered that the values of Pb, Cd, Cu, total dissolved solids (TDS), oil, and grease were beyond acceptable levels for human and ecological health. The study contributed to the inadequacy of existing management approaches and recommended the use of sophisticated treatment tools, including membrane filtration and reverse osmosis, to minimize adverse socio-environmental impacts.

Similarly, Onyema et al. (2015) also indicated that the discharges of offshore produced water were high in Cu, Zn, Fe, TDS, hardness, and alkalinity, similar to offshore produced water. However, subsequent analysis by Onyema et al., (2016) and Senanu et al. (2023) have revealed general compliance with the standards established by the World Health Organization (WHO) and the National Environmental Standards and Regulations Enforcement Agency (NESREA) of Nigeria. In contrast, Chikwe and Okwa (2016, 2017) observed that the chemical oxygen demand (COD), biological oxygen demand (BOD), TDS, and heavy metals (HMs), such as Pb, Cd, and Cr, were significantly higher, showing that the levels of organic and inorganic pollution are considerable. Other offshore investigations conducted by Okogbue et al. (2017, 2018) included excessive total suspended solids (TSS), COD, BOD, and toxicity of Cu, Zn, and Ni, which are dangerous to the ecosystem and population of the marine domain.

These findings underscore the need to conduct continuous and place-specific surveillance of heavy metals in produced water, in particular, due to the geochemical variability at the reservoir level (Chernysh et al., 2024), and the operation-specific nature in different fields (Ahmed et al., 2024; Onuh et al., 2021; Sj et al., 2024). Therefore, good characterization and treatment strategies should be reconsidered periodically during the entire lifespan of oilfield activities (Akbari, 2025).

Within the framework of the existing guidelines for conducting environmental evaluations of oilfields, this study examines the possibility of metal contamination at a particular location in the Niger Delta, which can be investigated by determining the concentrations of Pb, Cd, Zn, Fe, Cr, and Cu in the produced water samples. This is to assess the associated health and environmental hazards, expanding the methodology applied by Okogbue et al. (2018) in similar facilities in the region.

2. Materials and Methods

2.1. Description of Study Area

The research was undertaken in two different facilities located in fields F1 and F2 within the Delta state, in the north-western region of the Niger Delta. The topography is characterised by mangrove swamps cut by the Benin River. To avert conflicts of interest and abide by confidentiality terms in this study, the actual site of the oil and gas production plant is not shown on the map. The town where this production site is located is indicated on the map (Warri). Literature results necessitated this study area, as most of the heavy metal concentration assessment associated with produced water was done predominantly in the south-eastern region and the port-harcourt environs, thereby necessitating the need to ascertain the possible proportion of HMs in the produced water at that given time and space when sampling was done in this region, and how human and environmental exposure to such hazards may be harmful to health and aquatic life, as similarly reported by Ibekwe (2023) in another region. A map of the study area map and its environment are shown in Fig. 1 (Agbakwuru 2011).

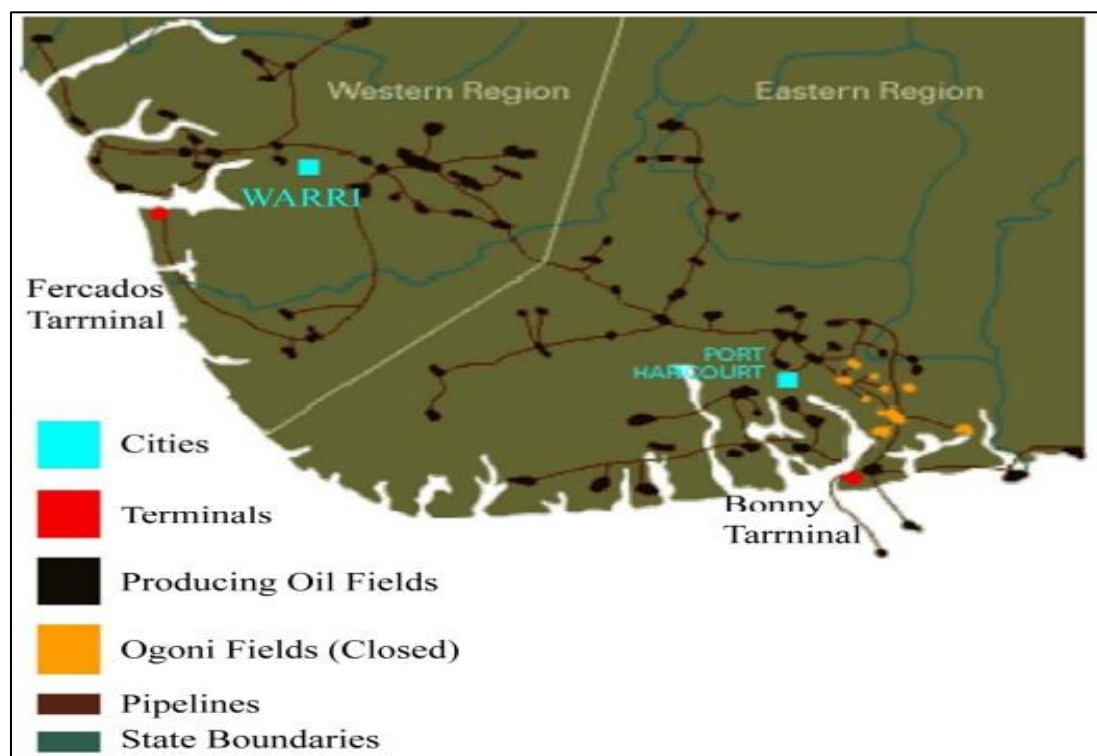


Figure 1 A map showing some oil fields, pipelines and the sampling location (Warri, Nigeria (Agbakwuru, 2011))

2.2. Sampling and Sample Preparation

The produced water extracts were obtained from separate oil and gas processing facilities in the oil-rich Niger Delta region of Nigeria. The method of targeted-sampling was applied, in which considerations were made based on production capacity, geographic area, and the availability of particular petroleum reserves. Aseptic high-density polyethylene (HDPE) containers were used to collect the samples to prevent contamination and maintain the integrity of the sample, as the bottles were chemically compatible with the analyte of interest. Each sample received an exclusive identification code, the date and time of collection, and the location of collection. Sampling was performed within a specified time to consider variations in the production schedules and operating conditions, thereby making the collected data reliable. To consider the potential spatial variation in the water quality and concentration of the constituents in the production system, some time interval was maintained before the produced water was collected from the separator tank for sampling.

2.3. Preservation and storage of samples

The storage and transportation of the produced water samples were performed using preservation techniques that did not cause the original properties of the samples to be lost. Various preservation methods were followed, subject to the type of analysis adopted. The samples were acidified further using hydrochloric acid to obtain a pH of 2. After preservation, each sample was properly sealed to ensure that it did not leak or become contaminated during conveyance to the Multidisciplinary University of Ibadan Central Research Laboratory. Various steps before treatment were also followed to ensure the accuracy of the analysis and removal of interferences. The immiscible phases were centrifuged before treatment and the suspended particles and debris were removed by filtration.

2.4. Heavy metals investigation

Individual heavy metal content was determined using Atomic Absorption Spectrometry (AAS). This is related to the observation of light absorption by metal atoms in a vaporized state. A wavelength of light appropriate to the metal of interest was passed through the samples, and absorption was measured. The extent of absorption is proportional to the concentration of the metal present, which allows for the quantification of heavy metals in the produced water. This method consists of three steps: atomization, absorption, and detection of the sample. Initially, the produced water

samples were pre-treated by suitable pre-treatment methods, including filtration and digestion, for the solubilisation of heavy metal species present in the water matrix.

In AAS, the samples to be analyzed were atomized by evaporating the species into a free atomic state in the vapour phase. This was done by flame atomization, in which the sample was fed into a high-temperature flame, in the case of our experiment, a nitrous oxide-acetylene flame. The high temperature dehydrates the solvent and can selectively decompose all molecular species, reducing the metal ions to free atoms. The absorption step was performed using a light source that emitted a certain wavelength of light specific to the metal being analyzed. A beam of light bounced off atomized samples A and B, and the metal atoms in the vapour phase absorbed energy at certain wavelengths, indicative of their electronic transition. The absorption of light was directly proportional to the metal in sample A and B. The last step is light detection and attenuation of the consumed light. The decrease in the intensity of the specific wavelength of light passing through atomized samples A and B was measured using a detector. The instrument measured the decrease in the intensity and compared the results with a calibration curve prepared using standard solutions of known concentrations of the target metal. Thus, the concentrations of metallic elements in the produced water in samples A and B were measured.



Figure 2 Atomic Absorption Spectrophotometer (AAS) in use

3. Result and Discussion

To determine the concentration of HMs in petroleum-produced water samples A and B and the corresponding impact on the environment with attendant risks associated with petroleum production within the Niger Delta region, the samples collected from this region were evaluated and interpreted using standardised parameter measurements.

3.1. Statistical Analysis of Heavy Metal Composition

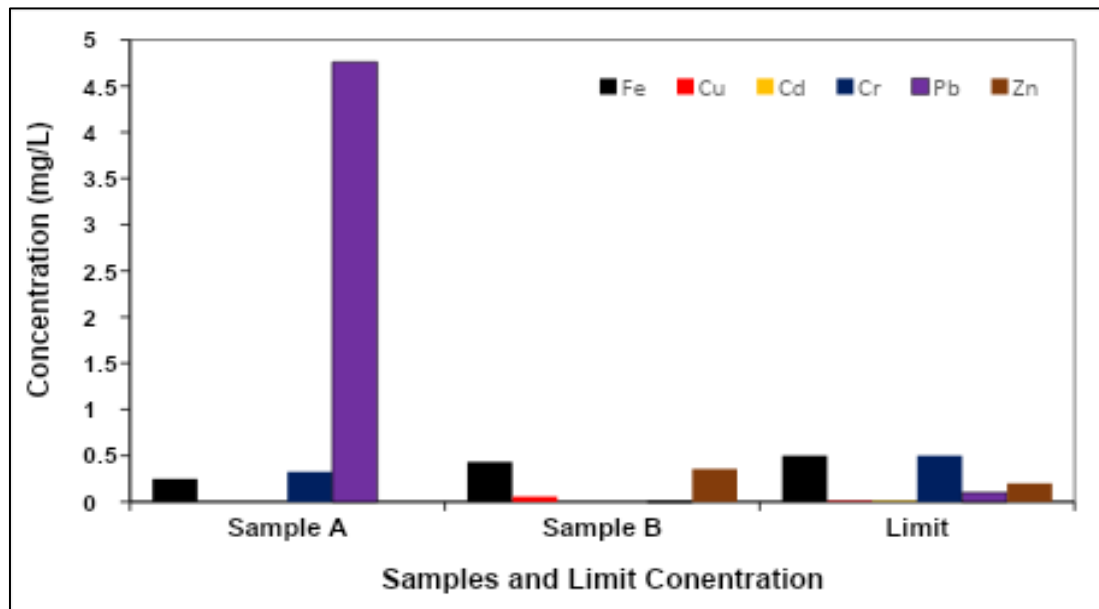
Statistical analysis of HMs concentrations in petroleum-produced water generated from petroleum prospecting and extraction in the Niger Delta must be thoroughly understood to determine harmful concentration thresholds for both humans and the environment. Detection of the HMs concentration threshold is fundamental to both the regulation and establishment of clean-up or treatment protocols. The results of absorption spectrometry are presented in Table 1.

Table 1 Results from Atomic Absorption Spectrometry

Heavy Metal	Sample A Concentration (mg/L)	Sample B Concentration (mg/L)	Limit Concentration (mg/L)
Fe	0.248	0.432	0.5
Cu	0	0.057	0.01
Cd	0	0	0.01
Cr	0.325	0	0.5
Pb	4.76	0	0.1
Zn	0	0.356	0.2

A comparative analysis was performed to determine the variability in the composition of the heavy metals across the samples. The t-test and Mann Whitney U test were used to compare and contrast the concentrations of HMs in samples A and B according to the underlying distribution of the data, as summarized in Figure 3. The significance level adopted was 0.05, to define whether differences between the groups were statistically significant. In addition, the concentrations obtained were compared to the set regulatory limits to determine compliance. When these limits are exceeded, it signifies that there are possible environmental hazards and that remedial or mitigation efforts are required. Correlation analysis was conducted to identify any correlation or connection between the heavy metal concentrations in the produced water samples. Statistical analyses were performed using the Excel statistical tool. The results of the statistical analysis were tabulated, illustrated, and summarized statistically for an integrated understanding of the heavy metal content of the produced water samples.

3.2. Descriptive statistics of HMs concentration

**Figure 3** Heavy metal concentration by sample and their limit of concentration

A descriptive statistical analysis of the obtained data was carried out to determine the heavy metal (Fe, Cu, Cd, Cr, Pb, and Zn) concentrations in samples A and B, and to determine if they were within the permissible concentration range, as illustrated in Figure 3. The Fe concentration in sample A was 0.248. This value was less than 0.5, which is the prescribed limit; therefore, the concentration of Fe in sample A was acceptable. In addition, the Cu concentration of Sample X was found to be 0, which was lower than the 0.01 limit. Thus, it can be concluded that the Cu concentration in Sample A was well below the stipulated concentration level. The Cd concentration in sample A was 0, which is consistent with the limit of 0.01. This result indicates that Cd from Sample A has negligible concentration and does not create a problem. Thus, we have Cr with a concentration of 0.325, which is lower than the limit of 0.5, for Sample A. Therefore

the Cr content of sample A was within an acceptable range. However, the concentration of Pb in Sample A was above the threshold value of 0.1 by having a concentration of 4.76. This result is an area of concern regarding any impact of Pb contamination on Sample A and should be investigated and appropriate remedial action should taken. Finally, Sample A had a Zn concentration of 0, which was within the allowed limit of 0.2. Therefore, according to the permissible standard, the concentration of Zn in Sample A did not pose any problems.

For sample B, the Fe concentration was determined to be 0.432, which was below the limit of 0.5. Hence, the Fe concentration in sample B was deemed to be within an acceptable range. Unlike Sample A, the Cu concentration in sample B was found to be 0.057, exceeding the limit of 0.01. This result highlights a potential issue with elevated Cu levels in Sample Y that should be addressed to ensure compliance with established standards. Similar to sample A, the Cd concentration in sample B was below the limit as no detectable Cd (0) was observed. Furthermore, the Cr concentration in sample B was measured as 0, aligning with the limit of 0.5. These findings suggest that sample B was unlikely to exhibit any significant concerns related to Cd and Cr contamination. In terms of Pb, the result for sample B showed a concentration value of 0, which is below the limit of 0.1. According to the results, it can concluded that there was no Pb contamination in sample B. Sample B had a Zn concentration of 0.356 within the acceptable range of 0.2. Based on this, the level of Zn in Sample A did not raise any environmental or health concerns within the stipulated standards.

3.3. Correlation analysis of heavy metal concentration

Determining the relationships between variables is also important when evaluating the impact of heavy metal concentrations. In this analysis, we considered the correlation between the heavy metal concentrations in samples (Sample A and B) of heavy metals. Correlation analysis provides extensive information about the distribution relationship between two different heavy metals and may help us identify patterns or trends in their concentrations. The following heavy metals were measured: Fe, Cu, Cd, Cr, Pb and Zn. Pearson's correlation coefficients were used to determine the strength and in what direction of the relationships between variables.

Table 2 Correlation coefficients of concentrations

Correlation Coefficient (r)	
Heavy Metal Concentration – A & B	-0.34
Radionuclide Concentration – A & B	0.84
Metal & Radionuclide Concentration - Sample A	1.00
Metal & Radionuclide Concentration - Sample B	0.50

The coefficient of correlations lie between -1.00 and +1.00 with -1.00 pointing to the occurrence of an optimal negative correlation, 0.00 to the absence of correlation, and +1.00 to the occurrence of an optimal perfect positive correlation. The correlation coefficient of the heavy metal concentrations between samples A and B was -0.34, as shown in Table 1. This negative value implies that the relationship is negative, that is, as heavy metal concentrations are high in sample A, the same is low in sample B, and vice versa. This implies that there may be an antagonistic relationship between the two heavy metal samples.

However, it is also noteworthy that correlation does not imply causation, and additional research will be necessary to determine whether there are any causal relations between the concentrations that were determined. This analysis provides a basis for future studies and highlights the importance of measuring and controlling heavy metal levels in the environment.

4. Conclusion

According to the descriptive statistical analysis, the proportions of HMs (Fe, Cu, Cd, Cr, Pb, and Zn) in samples A and B were different. While Sample A showed an elevated level of Pb concentration above the prescribed limit, Sample B showed an elevated concentration of Cu above the prescribed limit. Therefore, some remediation work is recommended for Pb contamination in sample A and high Cu in sample B to meet the relevant compliance standards. Safeguarding human health and environmental quality requires constant monitoring and assessment of the level of activity. In

addition, comparisons to applicable regulatory limits and recommendations should be made to determine whether additional actions or mitigation measures are needed to reduce potential risks.

The analysis is based only on a small sample size of two samples (A and B), which may not be representative of the population or system being investigated considering the small sample size and small number of available sampling points. This implies that with a larger sample, we would be better able to draw stronger conclusions. Furthermore, in the descriptive statistical analysis, only the proportions of metallic contaminants in the samples and their comparison with limits were considered. While this is good information regarding compliance, it cannot determine certain crucial information, such as where the contamination is coming from, potential health risk, or the environmental context in which the samples were collected. Therefore, further studies are needed to establish the implications of heavy metal concentrations found through contextual analysis.

It should also be noted that the limits may differ for different governing bodies or standards applicable to the study area. Therefore, it is important to follow relevant regulations and guidelines to determine the proportion of heavy metals.

Finally, the constraints of the present research must be considered when deciding the conclusion regarding the heavy metal levels of Samples A and B through descriptive statistical analysis. Future studies that utilize more sample sizes have a wider scope of influencing variables, and adhering more to the parameters of available regulations will provide a broader picture of the presence of HM pollutants in the study area.

Based on this study, it is clear that analysis of the concentration of heavy metallic element contaminant in the produced water of the Niger Delta region highlights the necessity of providing efficient mitigation measures to reduce health risks and environmental safety. Based on the results obtained in this study, the following suggestions can be made as possible mitigation measures:

Enhanced Monitoring Programs: It necessary to create long-term and regular monitoring programs related to the monitoring of heavy metal levels in produced water. This must encompass systematic sampling and analysis to monitor changes in contamination levels over time. In addition, incorporating a sophisticated monitoring system and remote sensing can effectively monitor the proportion of heavy metallic elements in produced water samples. Therefore, it is important to rapidly identify changes in heavy metal concentration in wastewater to facilitate the execution of contingency plans to prevent possible health and ecological hazards.

Environmental Impact Assessment (EIA) results should be used in decision making for location selection, adoption of adequate mitigation measures, and compliance with environmental regulations.

Research and development programs should focus on increasing the understanding of heavy metal distribution, behaviour, and transport in produced water systems at surface and subsurface oil and gas production facilities. Research must also be conducted on new technologies for heavy metal removal, processing, and disposal. Academic-industrial and academic-government research partnerships will also contribute to gaining a better understanding of this problem, ultimately enabling better mitigation strategies.

Compliance with ethical standards

Acknowledgments

The University of Ibadan's Central Research Laboratory was a vital contributor to the process that resulted in the publication of this research paper, and the author is grateful for their assistance in providing facilities and equipment for the experimental investigation.

Disclosure of conflict of interest

The authors declare the absence of any conflicts of interest connected to this study

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