



Evaluation of total petroleum hydrocarbon(TPH) in groundwater in the Niger Delta region of Nigeria.

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Abstract.

Groundwater is a crucial component of the global hydrological cycle often referred to as water stored within geological formations beneath the Earth's surface. This subsurface water reservoir is pivotal in maintaining ecological balance and supporting various life forms. While water is generally abundant in nature, finding high-quality water suitable for human consumption remains a pressing global challenge. This scarcity underscores the critical importance of water as a vital natural resource. This study investigated how crude oil pollution affects groundwater quality in an Oil and Gas host community in Rivers State, Nigeria. Groundwater samples were taken from boreholes in Obrikom community and analyzed for Total Petroleum Hydrocarbons (TPH). Results obtained are compared with the European Union Environmental Protection Agency (EUEPA) and Nigerian Upstream Petroleum Regulatory Commission (NUPRC) Intervention standards. The extraction of the TPH was done by liquid-liquid extraction method using dichloromethane (DCM). Estimation of Total petroleum Hydrocarbon in groundwater sample was done using a Gas Chromatography Flame ionization detector (GC-FID). Results from the laboratory analysis of Total petroleum Hydrocarbon (TPH) of groundwater sample show that the mean concentration of TPH (444.20µg/L) was above EUEPA but less than NUPRC standards. The study shows that four of the five groundwater samples exceeded the stringent reference standard (EUEPA Limits 2009). Sample GW2 had the highest TPH value followed by GW4, GW3, GW5, and GW1. Hence it can be inferred that TPH pollutes the groundwater in the Obrikom community from crude oil. Groundwater pollution in this community might be as a result of crude oil processing facilities that litter the environment. The evaluation of total petroleum hydrocarbons (TPH) in groundwater in the Niger Delta region of Nigeria highlights the environmental impact of oil spills and leakage, which does not only contaminate local water sources but also exacerbates public health concerns. As climate change intensifies, increased rainfall and flooding can further mobilize these petroleum hydrocarbons, leading to broader contamination and greater vulnerability of ecosystems and communities already affected by oil-related activities. Urgent action to ensure a standard water treatment plant for the community should be a foremost action. Public awareness and sensitization campaigns are fundamental to combating groundwater pollution and educating communities about the risks and consequences of groundwater pollution.

Key Words: Groundwater, Crude oil, Total Petroleum Hydrocarbon, Climate Change.

1. Introduction.

The importance of water to the survival of human beings, livestock, and other living organisms cannot be overemphasized. Drinking water is one of the most essential, unavoidable and vital natural resources needed for life's existence and man's survival (Ezugwu & Akhimien, 2022). Ordinarily, water is available in surplus quantity but quality water fit for human consumption is scarce. Groundwater ordinarily refers to water inhabiting the voids found inside a geologic stratum. Water is principally classified into surface water and groundwater. Surface water refers to oceans, rivers, ponds, lakes, streams, and wetlands while groundwater is present below the earth's surface where it is stowed in porous soils and rocks (Nsi et al., 2022)

Uncontaminated natural groundwater in geological formations is original and suitable for use in both domestic and industrial purposes without a need for purification, a narrative that has unfortunately been changed by the industrial age as exemplified by oil exploration in many climes. Groundwater is a highly treasured natural resource for the sustenance and development of economic, social, and health matters as well as ecological multiplicity. It is an immeasurable natural resource that is exposed to natural and human impacts. Little attention was paid to the protection of groundwater quality for a long time as people were oblivious to the dangers carried on this critical resource and thus the impression that the geological environment protects groundwater quality succeeded for a period. Even though the physical environment offers some level of protection for groundwater system, pollutants still find their way into drinking water aquifers by permeating through the soil profile, and in most often transporting the contaminants to other aquifers in the direction of groundwater flow (Ugwoha & Omenogor, 2017).

In Nigeria and some other developing countries, the availability of safe drinking water is a long-standing concern. Water pollution is generally caused by the introduction of waste or toxic materials into the environment owing to several anthropogenic activities. The concern for clean and drinkable water is significant because it is essential to the entire ecosystem; thus, the quality of water that is available for utilization is of the essence. Groundwater pollution has been on the increase especially in both in the cities and communities with lots of industrial activities, population growth, poor sanitation, exploration and exploitation of crude oil. Groundwater usually flows toward water bodies and boreholes but the flow of groundwater in aquifer does not always reflect the flow of water on the surface (Dami *et al.*, 2013).

2.0 Materials and Method

- i. Silica gel (100/200 mesh size) (Fisher Scientific, New Jersey, USA)
- ii. Distilled Water (Organic free)
- iii. Hexane (CDH, India)
- iv. Sodium Sulphate (granular, anhydrous) (Loba Chemie PVT Ltd)
- v. Dichloromethane (JDH, China)
- vi. TPH standard solutions (AccuStandards),
- viii. Sulphuric Acid (JDH, China)

- xi. Nitric Acid (CDH, India)
- xii. Perchloric Acid (Fisher Scientific, USA)
- xiii. Gas Chromatography-Flame Ionization Detector (GC-FID) (Agilent, 7890A)
- xv. Separatory Funnels-1L with polytetrafluoroethylene (PTFE) stopcock
- xx. Vials-2ml with PTFE-lined screw caps
- xxi. Sonicator (MRC, USA)

The groundwater sampling procedure for this research adhered to globally accepted best practices and stringent international scientific protocols. These methodologies, employed by renowned researchers and experts, have significantly contributed to advancing our comprehension of the environmental consequences of oil contamination of groundwater resources. To guarantee the reliability and accuracy of the research outcomes, water samples were collected from five carefully selected boreholes within the Obrikom area. Each sampling site's exact geographic position was meticulously documented using cutting-edge GPS technology, as illustrated in Table 1."

Table 2.0: SAMPLE LOCATION AND GEOGRAPHICAL COORDINATES

S/N	SAMPLE CODE	SAMPLE TYPE	SAMPLE LOCATION	GEOGRAPHICAL COORDINATES	
				Latitude.	Longitudde.
1	GW1	Groundwater	Obrikom community	5.400584	6.674793
2	GW2	Groundwater	Obrikom community	5.398844	6.669669
3	GW3	Groundwater	Obrikom community	5.395706	6.664185
4	GW4	Groundwater	Obrikom community	5.393411	6.664329
5	GW5	Groundwater	Obrikom community	5.389401	6.670735

2.1 TPH Analysis of Water Samples

2.1.1 Clean-Up Extraction and Clean-Up of TPH in Water Sample

Analysis of the water samples was done by liquid-liquid extraction method where dichloromethane (DCM) was used as the extracting agent. Each water sample was measured and 100ml of each sample was pipette into a separating funnel. Since 1 ml of surrogate standard O-Terphenyl was added to each sample, the sample was mixed by shaking the funnel for 1-2 mins with interim venting. The organic layer was left to settle from the water phase for at least 10 min and the organic layer was later transferred to a flask. The process of extraction was done thrice and the extract and collected in an Erlenmeyer flask. The extracts were dried with anhydrous sodium sulphate and later concentrated to 2ml via a rotary evaporator and purified using silica gel column chromatography to rid the samples of any interferences. Hexane in the proportion of 25ml was used to elute the TPH components from the column into a flask. The eluent obtained from the column chromatography was further concentrated to 2mL and this was done by gently bubbling Nitrogen gas through it. Last of all, the concentrated TPH extract was transferred into a gas chromatography injection vial as it was prepared for GC analysis using the equipment.

2.1.2 GC/FID Analysis of TPH Extract

The the collected TPH extract was evsluated using the by Agilent HP 7890A Gas Chromatography-FLame Ionization Detector (GD-FID). Before the actual analysis, the equipment was conditioned with TPH standard solutions (AccuStandards), at the exact inlet, oven and detector temperatures and timings. To ascertain that the acceptance criteria had been achieved in calibration, the verification was done and for sample injection and analysis, the relative standard deviation was done and did not exceed 20%. The sample was then injected using a micro syringe through the autosampler to the GC column to distinguish different compounds in the sample. The FID, after the separation, analyzes of the different compounds that are contained in the sample. Qualitative determination of the compounds of the mixture was done based on the peak recognition technique where the retention time of the standard was compared to that of the analyte from the sample. If one has identified the target compound of interest, then the calculation of the amount of that compound in the sample would be approximated by a value determined from the integration of both the resolved and the unresolved peaks in the chromatogram generated by the software of the instrument.

3.0 Result.

Table 3.0: Aliphatic components (C9 -C40), their mean across the five samples

Aliphatic Components (µg/L)	SAMPLE ID					mean	EUEPA Limits: 2010	NUPRC Intervention Limits: 2019
	GW1	GW2	GW3	GW4	GW5			
n-Nonane (C9)	ND	ND	ND	ND	ND		-	-
n-Decane (C10)	49.02	14.16	ND	2.45	4.45	17.52	-	-
n-Undecane (C11)	ND	4.37	ND	3.98	7.26	5.20	-	-
n-Dodecane (C12)	9.27	44.09	1.71	ND	13.51	17.14	-	-
n-Tridecane (C13)	ND	2.76	5.81	4.79	11.98	6.34	-	-
n-Tetradecane (C14)	18.11	55.64	ND	51.76	37.98	40.87	-	-
n-Pentadecane (C15)	ND	4.41	16.35	4.04	4.57	7.34	-	-
n-Hexadecne (C16)	17.10	41.40	21.58	84.75	61.59	45.29	-	-
n-Heptadecane (C17)	ND	4.74	40.46	2.91	ND	16.04	-	-
Pristane	1.14	8.1	1.25	2.07	2.52	3.01	-	-
n-Octadecane (C18)	15.52	10.3	42.07	81.16	62.20	42.25	-	-
Phytane	7.45	28.0	7.75	9.95	2.61	11.16	-	-
n-Nonadecane (C19)	ND	13.2	ND	1.58	8.61	7.81	-	-
n-Eicosane (C20)	11.16	24.3	74.43	62.03	ND	42.98	-	-
n-Heneicosane (C21)	9.83	13.0	ND	3.20	ND	8.67	-	-
n-Docosane (C22)	17.45	19.5	60.52	38.96	31.14	33.52	-	-
n-Tricisane (C23)	ND	22.4	ND	3.81	ND	13.12	-	-
n-Tetracosane (C24)	12.75	59.7	52.11	27.88	ND	38.11	-	-
n-Pentacosane (C25)	16.98	82.9	44.23	7.52	4.54	31.24	-	-
n-Hexacosane (C26)	9.24	25.5	45.63	13.73	10.37	20.90	-	-
n-Heptacosane (C27)	8.90	21.8	ND	9.18	5.16	11.25	-	-
n-Octacosane (C28)	9.68	23.9	41.23	12.87	7.17	18.97	-	-
n-Nonacosane (C29)	12.04	27.8	ND	6.25	4.39	12.63	-	-
n-Triacontane (C30)	ND	13.2	ND	6.74	5.30	8.41	-	-

n-Hentriacontane (C31)	11.47	19.7	ND	9.91	5.48	11.63	-	-
n-Dotriacontane (C32)	ND	10.6	ND	4.04	5.01	6.54	-	-
n-Tritriacontane(C33)	ND	18.9	7.48	4.53	4.71	8.89	-	-
n-Tetracontane (C34)	ND	12.7	ND	21.97	21.58	18.75	-	-
n-Pentatriacontane (C35)	ND	ND	2.34	5.90	5.76	4.67	-	-
n-Hexatriacontane (C36)	11.90	12.5	ND	20.87	ND	15.10	-	-
n-Heptatriacontane (C37)	ND	9.4	3.04	ND	5.32	5.92	-	-
n-Octatriacontane(C38)	ND	ND	ND	4.68	ND	4.68	-	-
n-Nonatriacontane (C39)	ND	ND	ND	3.62	ND	3.62	-	-
n-Tetracontane (C40)	ND	ND	ND	4.61	ND	4.61	-	-
Total TPH (µg/L)	249.01	649.06	467.97	521.75	333.22	444.20	300	600

Table 3.1: Total TPH, the mean across five samples in comparison with standard references.

	SAMPLE ID					mean	EUEPA Limits: 2010	NUPRC Intervention Limits: 2019
	GW1	GW2	GW3	GW4	GW5			
Aliphatic Components (µg/L)								
Total TPH (µg/L)	249.01	649.06	467.97	521.75	333.22	444.20	300	600

Figure 3.0 below shows Total Petroleum Hydrocarbon for the five groundwater samples. Sample GW2 has the highest TPH value followed by GW4, GW3, GW5 and GW1. They all exceed the stringent reference standard (EUEPA Limits 2009) except GW1. However, using Nigeria standard (NURPRC, 2018) as reference only groundwater sample GW2 can be said to exceed the reference limits. The minimum combine Aliphatic compound was found in groundwater sample GW1 with a concentration of 249.005(µg/l) and the maximum combine aliphatic compounds was found in groundwater sample GW2 with a value of 649.062 (µg/l). This can be attributed to the nearness of the sample point to the Obrikom river which is always impacted with crude oil spillage due to illegal bunkering activities. These values are indication that the ground water likely polluted by crude oil. The high levels of total petroleum hydrocarbon contamination observed in this study are comparably higher than the levels obtained by Olver, (Alinnor,2014) where the overall level of TPH recorded in their study in the petroleum contaminated site. Total Petroleum hydrocarbon in groundwater due to crude oil pollution poses significant health risks to humans. Petroleum-derived hydrocarbon mixtures, commonly referred to as Total Petroleum Hydrocarbons (TPH), are complex organic substances present in crude oil that can be quantified in various environmental mediums. These

hydrocarbon compounds are composed of numerous fractions derived from petroleum (ASTDR, 1999). Total Petroleum hydrocarbons (TPH) are pure carbon and hydrogen-based chemical entities; they encompass a wide array of hydrocarbon molecules varying in molecular mass Owhonda et al., (2021). The carcinogenic, neurological, reproductive, cardiovascular, and respiratory impacts of TPH exposure can be severe and long-lasting, especially for vulnerable populations such as children and pregnant women (Adipah, 2019). Prompt action to address groundwater contamination and prevent further exposure is crucial to mitigate these health risks and protect public health. Total Petroleum Hydrocarbons (TPHs) pose significant threats to human health, like stomach aches, cramps, nausea, diarrhoea, and vomiting (Uzobo et al., 2023) .

Prolong exposure to TPHs can lead to numerous health issues, including skin and eye irritation, respiratory problems, neurological effects, (Kuppusamy et al., 2020: Erifeta, et al., 2023). Cleaning workers at oil spill sites face heightened risks due to prolonged exposure. Key factors influencing the severity of health impacts include the duration and intensity of exposure. Direct contact with contaminated substances increases the risk of adverse health outcomes. Health protection measures are crucial for individuals exposed to TPHs, emphasizing the need for comprehensive risk assessments and monitoring programs. Kuppusamy et al., 2020)

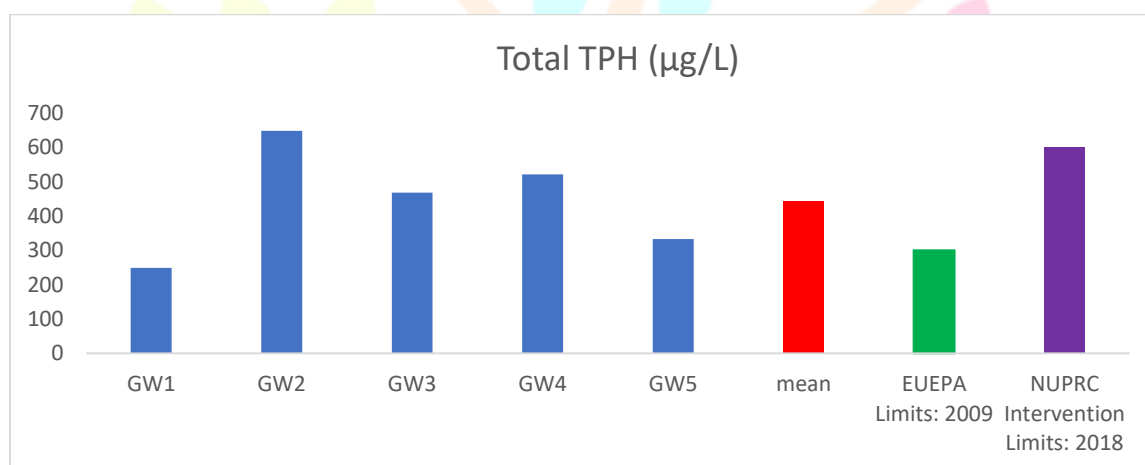


Figure 3.0: COMPARATIVE CHART OF GROUNDWATER TPH VALUE, ITS MEAN VALUE WITH STANDRAD REFERENCE

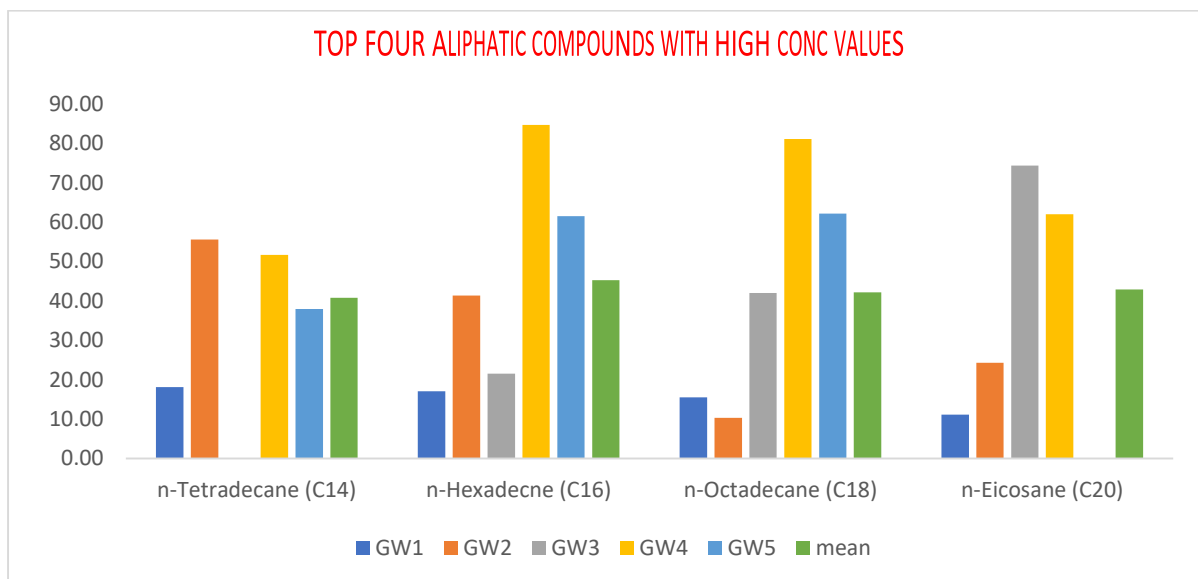


Figure 3.1 CHART OF TOP FOUR TPH COMPONENTS (ALIPHATIC COMPOUND) WITH HIGHEST CONCENTRATION VALUES IN SAMPLED COMMUNITY GROUNDWATER.

CONCLUSION

This study highlights the significant impact of crude oil pollution on groundwater quality in the Obrikom community, Rivers State, Nigeria. The analysis of Total Petroleum Hydrocarbons (TPH) revealed contamination levels that exceed the stringent European Union Environmental Protection Agency (EUEPA) standards, although they remain within the limits set by the Nigerian Upstream Petroleum Regulatory Commission (NUPRC). The findings suggest that crude oil-related activities, particularly from processing facilities, are a primary source of groundwater contamination. Given the essential role of groundwater for human consumption and ecological balance, it is critical to implement urgent measures, including the installation of a standard water treatment facility and raising public awareness about the dangers of groundwater pollution. These actions are necessary to protect public health and preserve groundwater resources in the community.

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