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Assessment of Petroleum Hydrocarbon and Heavy Metal Contamination of Ground Water Resources Around Some Retail Fuel Dispensing Stations in Ojo Local Government Area, Lagos, Nigeria

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ABSTRACT

The study pursues to appraise the status of groundwater around fuel stations in Ojo Local Government Area of Lagos state, Nigeria. Water samples were gathered from 10 non-identical locations around a fuel station in the study area. Physico-chemical criteria: biological oxygen demand (BOD), pH, chemical oxygen demand (COD), colour, electrical conductivity, total dissolved solid (TDS), and total petroleum hydrocarbon (TPH) were analyzed. Also, heavy metals (Zn, Fe, Pb, Ni and Cd) concentrations of the water samples were investigated using Atomic Absorption Spectrophotometer (AAS). Measured pH (4.3-6.5) for the water in this study revealed weakly acidic water. The electrical conductivity was within the range of 340 and 1000 µScm⁻ ¹. Other physico-chemical parameters such as TDS, TPH, COD and BOD, were within the range of 247-719 mg/L, 0.01-0.10 mg/L, 28.66-44.22 mg/L, and 16.86-26.01 mg/L values respectively. Zn, Fe, Pb, Ni and Cd were detected in water samples with mean concentrations scores of 0.245, 0.413, 0.007, 0.017 and 0.003 mg/L respectively. In this research work, the values for degree of contamination fell within the range of 0.31-1.04, the water quality index (WQI) values were within the range of 0.0009 -0.0019. Pollution index (PLI) values ranged from 0.2959-0.6332. From the result obtained in this study, petroleum residues and some heavy metals were present in the water samples, although not above the acceptable limits stipulated by WHO except for the case of Iron and Cadmium that were above the acceptable limit specified for drinking water in some of the water samples assessed in this study.

Keywords: Groundwater, Health assessment, Heavy metals, Pollution indices, Total petroleum hydrocarbon

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INTRODUCTION

Hydrocarbon products have highly contributed to energy needs across the world and growth of economy for countries producing oil (Ite et al., 2016). Ite et al. (2018) has described that both surface and groundwater can be contaminated by organic and inorganic chemicals, radionuclides, and/or microbes in places where petroleum production activities are carried out. Total petroleum hydrocarbons (TPH) released into the environment through anthropogenic activities or as by-products into the soil subsequently makes its way into the water aquifers (Adipah, 2019). Some of these TPH can be breakdown by some organisms into smaller fragments and of which some could sublime into the atmosphere, others could remain buried in the soil for a prolong time and could be utilized by other organisms in the soil leading to unhealthy situations (Nardini et al., 2010).

Water is expected to be of high quality and free from contaminants irrespective of what it is used for such as drinking and domestic purposes (Kwaya *et al.*, 2019). Impurities of both organic and in organic origin, dissolved in groundwater moves through the earth strata. The public are mostly exposed to contaminated water with malicious and harmful elements. Therefore, assessing water quality is of utmost importance to accurately evaluate the associated danger (Oden, 2012).

Heavy metals have been well known to be metallic elements that have high density and could be harmful even at low concentrations when they gathered with time within the body (Amadi *et al.*, 2016). Humans' wellbeing has been reported to be directly affected by effect of petroleum products spillage (Gwack *et al.*, 2012). Biological breakdown of petroleum hydrocarbons is tedious and challenging because of the existence of heavy metals, that are toxic toward most biodegrading microorganisms (Almeida *et al.*, 2013). This study evaluates the total petroleum hydrocarbons, heavy metal pollution indices and health assessment of ground water around fuel stations in Ojo Local Government Area of Lagos State, Nigeria.

METHODOLOGY

Study Location

This study covers some ground water sources around petrol filling stations in Ojo Local government area of Lagos State, Nigeria geographically located at longitude 3°11 E and latitude 6°28N

Study Design

The research involved an analytical phase that encompassed various steps, including environmental media analysis, gathering of samples, preparation, and laboratory work.

Sample Analysis

The samples were transferred to Biochemistry Drug laboratory of Lagos State University, Nigeria and kept under a temperature of 4°C in cold room. The samples underwent analyses for specific and pertinent physico-chemical criteria as well as heavy metals. The testing procedures followed the methods outlined in the Standard Methods for Examination of Water and Wastewater. (American Public Health Association (APHA), 2017).

Different physico-chemical criteria which include pH, electrical conductivity (EC), total dissolved solid (TDS), total petroleum hydrocarbon (TPH), chemical oxygen demand (COD) and biological oxygen demand (BOD) were investigated in the groundwater samples. Potentially toxic metals (cadmium, nickel, iron, lead and zinc) levels were evaluated by digestion; 50 mL of the well-mixed sample was transferred to a beaker and heated on a hotplate, avoiding boiling, until the volume was reduced to 15-20 mL. The process involved heating the sample for 30 minutes while adding concentrated nitric acid (15 mL). Afterward, the solutions were allowed to attain the room temperature and then meticulously filtered. The

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samples digested were maintained by adding deionized water to a 100 mL volumetric flask and then diluted to the desired volume. This process was carried out in duplicate, and the samples were further analyzed using the Perkin Elmer A Analyst 200 Flame Atomic Absorption Spectrophotometer.

Contamination Factor

Contamination factor (CF) is the water contamination level by metals (Syed *et al.*, 2012). It can be expressed using Equation (1).

$$CF = \frac{C_i}{B_i}$$
 Eqn. 1

Where C_i is the concentration estimation of a particular element in the sample of ground water and B_i is the concentration of the particular element in the background sample. The background sample is the WHO upper limit standard for concentration of element in drinking water (Edori *et al.*, 2016).

For degree of contamination (dC), Hakanson (1980) suggested these categories: dC < 6 illustrate a contamination of low-level status;6 < dC < 12 is a contamination of moderate-level status; 12 < dC < 24 is a contamination of considerable-level status; and dC > 24 is a contamination of high-level status, exhibiting acute anthropogenic contamination.

Water Quality Index

The unit weight of a particular element (W_i) is calculated using Equation 2 (Olatunji *et al.*, 2015).

$$W_i = \frac{K}{B_i}$$
 Eqn. 2

Where B_i is as defined in Equation (1). *K* is a constant of proportionality which is taken to be unity for simplicity (Olatunji *et al.*, 2015). The water quality index (WQI) is estimated using Equation 3.

$$WQI = \frac{\sum (CF \times W_i)}{\sum W_i}$$

Eqn. 3

Where *CF* is as defined in Equation (1). The numerical value of WQI less than 1 implies that the water is fit for drinking and a numerical value higher than or equivalent to 1 exhibit that the water is unfit for drinking (Bangalore and Latha, 2008).

Pollution Load Index

The pollution load index (PLI) is presented in Equation 4, and it seeks to provide a quantification of the level of all-inclusive pollutants at a sampling location (Mmolawa *et al.*, 2011). Additionally, it is employed for pollution detection, enabling the comparison of pollution levels across various locations and time periods (Syed *et al.*, 2012). The PLI gives a measure of the metal pollution state. A PLI measure lower than 1 denotes the water is not contaminated, a PLI measure of 1 means only the baseline level of pollution is present and a PLI measure higher than 1 indicates the water is contaminated.

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times \dots CF_n}$$
 Eqn. 4

Data Analysis

The heavy metals data were processed using SPSS version 24 to calculate the mean and standard error of the mean. Subsequently, statistical significance tests were conducted using ANOVA (p<0.05). For those results that exhibited statistical differences, a Tukey's post hoc analysis test (post ANOVA) at p<0.05 was applied. This was carried out to ascertain whether there were statistical disparities in the mean any concentrations of heavy metals in the underground water samples across the ten locations.

RESULTS AND DISCUSSION

The locations and physico-chemical criteria of the samples of water gathered are indicated in Table 1. The parameters captured were pH, electrical conductivity, TDS, TPH, COD and BOD.

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Groundwater is the water that fills the pore spaces or crevices in the subsurface of the Earth. It is a significant source of potable (drinkable) water in both rural and urban areas of Nigeria (Olatunji et al., 2015). Groundwater contamination is a significant global issue (Hazem and Talaat, 2017). Numerous studies have been conducted to investigate and address this problem (Afolayan et al., 2012; Akoteyan et al., 2011; Edori et al., 2016; Ernest et al., 2010; Idowu and Olubunmi 2013; Olafisoye et al., 2013; Olatunji et al., 2015; Olu et al., 2022; Olu and Iyere 2020; and Oyedami et al., 2013). In this study derived out of Table 1, recorded pH measures ranges between 5.40 and 6.50, and these values fall within the accepted ranges set by Bodrud-Doza et al. (2016) and World Health Organization (WHO) (2006, 2011). Measured pH for the water in this study revealed weakly acidic water.

The electrical conductivity was within the range of 340 and 1000 μ Scm⁻¹. Other physico-chemical criteria inclusive of total dissolved solids (TDS), total petroleum hydrocarbons (TPH), COD and BOD, were within the range of 247-719 mg/L, 0.01-0.10 mg/L, 28.66-44.22 mg/L, and 16.86-26.01 mg/L values respectively. The TDS of the samples of water investigated in this study was within the World Health Organisation standard (WHO, 2006, 2011). In like manner, the study by Salami *et al.* (2019) revealed TDS in twelve (12) different water samples ranging from 23-121

mg/L which also fall within World Health Organisation standard (WHO, 2006, 2011). In this study, the total petroleum hydrocarbon concentrations in water samples were below 10 mg/L which is the maximum acceptable standard set by the Federal Ministry of Environment in Nigeria (Clinton *et al.*, 2009).

The heavy metal level in each of the water samples are indicated in Table 2. The results of the study illustrate that the analyzed water samples contained detectable concentrations of several heavy metals, including zinc (Zn), iron (Fe), lead (Pb), nickel (Ni), and cadmium (Cd). The average concentrations of heavy metals in samples of water were: 0.245, 0.413, 0.007, 0.017 and 0.003 mg/L respectively. The concentrations of heavy metals analyzed in the samples from locations 2 and 5 were below the standard prescribed by WHO for drinking water. All the locations had Zn, Pb and Ni concentrations that were within the limit for drinking water. However, eight of the locations showed Iron limit above the limit standard as specified for drinking water.

The Pb levels from this study (0.006 -0.012 mg/L) were lesser than study reported by Addo *et al.* (2013), Boateng *et al.* (2015), Nassef *et al.* (2006), and Kortatsi (2007). On a contrary to the mentioned studies, the findings in this study were in consonant with those described by Wongsasuluk *et al.* (2014).

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Table	Table 1: Collected water sample locations and their physico-chemical characteristics										
Water	Geographical	рН	Electrical	TDS	TPH	COD	BOD				
sample	Location		conductivity	(mg/L)	(mg/L)	(mg/L)	(mg/L)				
			(µScm⁻¹)								
1	Latitude: 6.46617	6.00	590.00	420.00	0.02	35.22	20.72				
	Longitude: 3.19601										
2	Latitude: 6.47363	6.40	520.00	373.00	0.01	28.66	16.86				
	Longitude: 3.18505										
3	Latitude: 6.47721	5.70	340.00	247.00	0.03	39.78	23.40				
	Longitude: 3.18594										
4	Latitude: 6.48	5.80	470.00	337.00	0.09	33.13	19.49				
	Longitude: 3.18776										
5	Latitude: 6.48198	5.40	360.00	258.00	0.10	34.04	20.02				
	Longitude: 3.18812										
6	Latitude: 6.48743	6.00	590.00	422.00	0.10	31.45	18.50				
	Longitude: 3.19113										
7	Latitude: 6.48772	6.10	720.00	573.00	0.04	44.22	26.01				
	Longitude: 3.19894										
8	Latitude: 6.48669	5.70	540.00	386.00	0.06	42.16	24.80				
	Longitude: 3.19966										
9	Latitude: 6.49093	5.70	620.00	445.00	0.07	41.96	24.68				
	Longitude: 3.19908										
10	Latitude: 6.49255	6.50	1000.00	719.00	0.08	35.85	21.09				
	Longitude: 3.19932										
SON ¹	-	6.5-8.5	1000	1000.00	10	-	-				
WHO	-	6.5-8.5	-	1000.00		-	-				
Standard ²											

Total dissolved solids (TDS), total petroleum hydrocarbons (TPH), chemical oxygen demand (COD) and biological oxygen demand (BOD)

1: Standard Organisation of Nigeria (SON), (2015)

2: WHO (2006)

Locations 4, 6, 8 and 9 had Cd concentrations that were above limit standards as specified by WHO for drinking water as indicated in Tables 2 and 3. Subjection to higher level of Cadmium (Cd) could hamper the kidney in addition to generating critical health impacts (Momodu and Anyakora,

2010; Olu et al., 2022). The average Cd concentration in this study was comparable to details by Kortatsi (2007), Asare-Donkor et al. (2015) and Boateng et al. (2015) on similar studies.

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Table 2: Heavy Metal concentrations (mg/L) in all samples collected								
Location	Zn	Fe	Pb	Ni	Cd			
1	0.094	0.491	0.009	0.012	0.001			
2	0.124	0.289	0.006	0.011	0.002			
3	0.099	0.311	0.009	0.009	0.003			
4	0.098	0.499	0.010	0.013	0.004			
5	0.248	0.361	ND	0.018	ND			
6	0.244	0.491	0.012	0.018	0.006			
7	0.346	0.391	0.006	0.019	0.002			
8	0.399	0.492	0.007	0.020	0.007			
9	0.486	0.384	ND	0.023	0.006			
10	0.361	0.424	0.010	0.022	0.003			
WHO	3	0.3	0.01	0.07	0.003			
Standard ¹								
SON ²	3	0.3	0.01	0.02	0.003			

Table 2:	: Heavy Meta	l concentrati	ions (mg/L) in	all samples	collected
	_	-			

ND- Not detected

1: WHO (2006, 2011)

2: SON, (2015)

The iron concentration in the groundwater from Table 2 ranged from 0.289 to 0.499 mg/L, with an average of 0.413 mg/L (Table 3). The acceptable limit of Fe concentration in groundwater is 0.3 mg/L as set by WHO (2011) classification. Twenty percent (20%) of the samples had lower Fe concentration than the maximum allowable limit.

Long term consumption of water with high level of iron could lead to weakness, loss of weight, joint pains and finally heart ailment, liver issues and diabetes (Olu et al., 2022). Research conducted by Ansa-Asare et al. (2009) indicate that the levels of Fe were excessive in contrast to this study.

Table 3: Descri	ptive statistics of	of overall sam	ples of water h	neavy metal levels
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Units/Element	Zn	Fe	Pb	Ni	Cd
Minimum	0.094	0.289	0.000	0.009	0.000
Maximum	0.486	0.499	0.012	0.023	0.007
Mean	0.245	0.413	0.007	0.017	0.003
SD	0.144	0.079	0.004	0.005	0.002
V	0.21	0.006	0.000	0.000	0.000
Skew	0.282	-0.318	-0.906	-0.258	0.259
Kurt	-1.397	-1.369	-0.120	-1.443	-1.064
WHO Standard ¹	3	0.3	0.01	0.07	0.003
SON ²	3	0.3	0.01	0.02	0.003

ND- Not detected, SD- Standard Deviation, V- Variance

1: WHO (2006, 2011)

2: SON (2015)

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Heavy metals contamination factor is illustrated in Table 4. The contamination factor (CF) in this study as shown in Table 4 for Zn is 0.031-0.162, Fe had a value of 0.963-1.663, Pb had a value of 0.6-1, Ni had a value of 0.013-0.329 and Cd had a value of 0.333-2.333. All the samples fall within the low contamination factor level class as indicated by Odunlami and Salami (2018).

Table 4. Containination factor for neavy metals in an sample conected								
Location	Zn	Fe	Pb	Ni	Cd			
1	0.031	1.637	0.9	0.171	0.333			
2	0.041	0.963	0.6	0.157	0.667			
3	0.033	1.037	0.9	0.129	1			
4	0.033	1.663	1	0.013	1.333			
5	0.082	1.203	ND	0.186	ND			
6	0.081	1.637	1.2	0.257	2			
7	0.115	1.303	0.6	0.271	0.667			
8	0.133	1.640	0.7	0.286	2.333			
9	0.162	1.280	ND	0.329	2.0			
10	0.120	1.413	1	0.314	1			

Table 4: Contamination factor for heavy metals in all sample collected

Table 5: Pollution indices for heavy metals in all samples collected

Location	Degree of	Water Quality	Pollution Load
	Contamination	Index	Index
1	0.61	0.0012	0.3050
2	0.49	0.0009	0.3018
3	0.62	0.0009	0.3308
4	0.84	0.0013	0.4224
5	0.31	0.0013	0.2959
6	1.04	0.0016	0.6066
7	0.59	0.0015	0.4391
8	1.02	0.0019	0.6332
9	0.75	0.0018	0.6082
10	0.77	0.0017	0.5567

Some pollution indices of the heavy metals present in the water samples are illustrated in Table 5. In this study the degree of contamination values was within 0.31-1.04 and location 6 had the highest value. All these values are very low degree of contamination as reported by Abrahim and Parker (2008).

When applied to heavy metal content data in water samples, correlation analysis can reveal patterns and associations between these metals, providing insights into their sources and pathways of contamination (Azaza *et al.*, 2011;

Parizi and Samani 2013). A high correlation coefficient (near 1 or 1) implies a nice positive connection between two variables and its value of zero connotes lack of connection between them at p < 0.05 significant level (Varol and Davraz, 2014). Accurately, criteria exhibiting r > 0.7 are connote to be intensely correlated while r that fell within 0.5 and 0.7 illustrates correlation with a moderate status (Manish *et al.*, 2006). Table 6 illustrates this research work in regard of heavy metals correlation matrix.

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Zn exhibits a negatively moderate correlation for Pb (r = -0.449, p > 0.05). Pb exhibits a negatively moderate correlation to Ni (r = -0.353 p > 0.05). Pb also exhibits a negatively moderate correlation to total petroleum hydrocarbons (TPH), COD and BOD (r = -0.057, -0.285 and -0.285 respectively, p > 0.05). Zn exhibits a positively high correlation for Ni (r = 0.944, p < 0.05). Cd exhibits a positively moderate correlation to Zn (r = 0.495, p > 0.05), Fe (r = 0.422, p > 0.05), Pb (r = 0.192, p > 0.05) and Ni (r = 0.412, p > 0.05). Except for the case of Zn and Ni, COD and BOD, all other heavy metals and physico-chemical parameters, indicate no significant correlation with other heavy metals, showing that their dispersion were not regulated by an identical variable. The robust correlations among certain heavy metals suggest common sources of origin and shared geochemical characteristics (Lu *et al.*, 2010; Saeedi *et al.*, 2012). Hence, the connection of metals with vagueness suggest that the groundwater has incorporated lots of pollutants from chemical industries operations, and sewage treatment plants (Boateng *et al.*, 2015).

		Zinc	Iron	Lead	Nickel	Cadmium	TDS	TPH	COD	BOD
Zinc	Pearson Correlation	1	.093	449	.944**	.495	.447	.345	.607	.607
Iron	Pearson Correlation	.093	1	.464	.268	.422	.264	.429	.026	.026
Lead	Pearson Correlation	449	.464	1	353	.192	.285	057	285	284
Nickel	Pearson Correlation	.944**	.268	353	1	.412	.556	.560	.424	.424
Cadmium	Pearson Correlation	.495	.422	.192	.412	1	.071	.302	.279	.279
Total dissolved solid	Pearson Correlation	.447	.264	.285	.556	.071	1	.089	.146	.146
Total petroleum hydrocarbon	Pearson Correlation	.345	.429	057	.560	.302	.089	1	110	110
Chemical oxygen demand	Pearson Correlation	.607	.026	285	.424	.279	.146	110	1	1.000**
Biological oxygen demand	Pearson Correlation	.607	.026	284	.424	.279	.146	110	1.000**	1

Table 6: Corre	lation coeff	icient matrix	of para	meters investi	gated in	groundwater	

**. Correlation is significant at the 0.05 level (2-tailed).

CONCLUSION

The groundwater around fuel stations in Ojo Local Government Area of Lagos state, Nigeria has been assessed and it has been shown from the results of this study that petroleum residues and some heavy metals were present in the water samples, although not above the limit stipulated by WHO except for the case of Iron and Cadmium that were above the acceptable limit required for

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drinking water in some of the samples of water assessed in this research work.

The degree of contamination, water quality index and pollution index of every sample of water gathered across the various locations were of low level of pollution and thus make the water in these locations healthy for consumption and domestic utilization.

There is need for continuous assessment of the groundwater around the fuel stations. Effective and cost friendly heavy metal treatment should be encouraged among the residents. Lastly, it will be better if the fuel station underground tanks are properly lined to prevent petroleum effluents from making their way into underground water source and regular checks should be carried out on the underground tanks.

AUTHORS' CONTRIBUTION

UNAEZE, C.H.: Developed experimental design of the research and the manuscript first draft.

MALLAM-DAUDA, M.: Involved in samples collection and manuscript development.

ANAGA, S.O..: Worked on the data analysis and edited the manuscript,

NOBLE-OKEREKE, H.: Involved in collection of samples and drafting of manuscripts

YUSUF, H.O.: Involved in the data interpretation and manuscript editing

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CONFLICT OF INTEREST

The authors conducted this study without any conflict of interest or biased motives.

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