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PETROLEUM POLLUTION AND WATER QUALITY IN THE PIPELINE RIGHT OF WAY LOCATED AT EFFURUN ROUNDABOUT, DELTA STATE, NIGERIA

AIMIUWU, E.E.,[1] EDEMA, O.M.,[1] *ISUKURU, E.J.[2] AND BIRMA, G.J.[3]
[1]Department of Chemistry, Federal University of Petroleum Resources, P.M.B. 1221 Effurun, Delta State, Nigeria.
[2]Department of Environmental Management and Toxicology, Federal University of Petroleum Resources, P.M.B. 1221 Effurun, Delta State, Nigeria.
[3]Department of Environmental Science and Management Technology, Petroleum Training Institute, Effurun, Delta State, Nigeria.
*Corresponding author: Isukuruefejeffery@gmail.com

Abstract
This study assesses the levels of petroleum pollution and its impact on the aquatic ecosystem around Effurun roundabout in Delta State, Nigeria. The distribution of n-alkanes and polyaromatic hydrocarbon (PAH) in surface water contaminated with crude oil and their implications for environmental and human health were analyzed. Total Petroleum Hydrocarbon (TPH) was determined using Gas Chromatography/Flame Ionization Detector (GC/FID). Four surface water samples were collected from the study area and one from the control site six months after an extensive oil spillage and petroleum-induced fire incidence in June 2016. The mean value of TPH obtained in surface water was 25.885±5.105mg/L. The study area had a significantly higher concentration of TPH than the control site. The concentrations of AHC, PAH, and PHC for the study area were recorded as 16.910±3.018, 8.944±2.122, and 25.885±5.105, respectively, while the concentrations of AHC, PAH, and PHC for the control samples analyzed were 1.716, 0.349, and 2.065, respectively. The study found positive correlations between aliphatic hydrocarbon and petroleum hydrocarbon concentrations, as well as between polyaromatic hydrocarbon and petroleum hydrocarbon concentrations, indicating similar sources and transport mechanisms for the pollutants. However, a weak positive correlation was found between aliphatic hydrocarbon and polyaromatic hydrocarbon concentrations, suggesting potential differences in sources and transport mechanisms. The study area is under pollution threat, and the clean-up done previously after the spill was insufficient to restore the integrity of the environment. The findings highlight the need for urgent remediation measures to prevent further damage to the ecosystem and to safeguard human health.

Key Words: *Crude oil pollution, water quality, n-alkanes, polyaromatic hydrocarbon, Effurun, Delta State*

Introduction

The contamination of water systems in the Niger Delta of Nigeria by petroleum hydrocarbons is a significant environmental issue with potential risks to human health and the environment. This research aims to assess the levels of petroleum pollution and its impact on the aquatic ecosystem. Petroleum hydrocarbons, which are organic compounds derived from crude oil or petroleum, are widely used in various industrial processes, transportation and energy production. The composition of these compounds is a diverse combination of hydrocarbons, with varying sizes and structures that range from minor molecules such as methane and ethane to larger ones like diesel, gasoline, and crude oil. The use of these hydrocarbons has brought significant benefits to human society, but it has also resulted in their release into the environment, causing significant threats to both human health and the environment (Inimino *et al*., 2020; Ukhurebor *et al*., 2021; Abayomi *et al.,* 2021; Abudu *et al*., 2022; Rakib *et al*., 2022). This research focuses on petroleum pollution in water systems, which is a significant environmental problem in the Niger Delta of Nigeria that has far-reaching implications. The study aims to determine the total petroleum hydrocarbon levels in surface water at Effurun Roundabout, Warri, Delta State, and assess the potential risks posed to human health and the environment. The findings of this study can contribute to the development of strategies for managing and preventing petroleum hydrocarbon contamination in surface water and can inform policymakers and relevant stakeholders on the potential risks posed by petroleum hydrocarbon contamination in surface water. Given the extensive water contamination caused by oil exploration in the Niger Delta, assessing the levels of petroleum pollution and its impact on the ecosystem is critical in mitigating the environmental and public health risks. This research's focus on the concentration of total petroleum hydrocarbons (TPH) in surface water emphasizes the need for action.

The environmental and public health risks posed by petroleum pollution in water systems are significant, with devastating effects on aquatic life and ecosystems, particularly in regions such as Nigeria's Niger Delta where oil exploration has caused extensive water contamination. Petroleum pollution in water systems is a significant environmental problem that has far-reaching implications. Hydrocarbons can contaminate water through direct spills or from spills that occur on land and subsequently reach water bodies. In Nigeria's Niger Delta region, oil exploitation by multinational companies has led to water contamination and environmental degradation (Akpan and Bassey, 2020). The contamination of water systems has had devastating effects on aquatic life-support systems and mangrove forests as hydrocarbons prevent oxygen transfer in the water column, even in small quantities (Onyena and Sam, 2020; Ahmed *et al*; 2021). Petroleum pollutants can render water unfit for human consumption, and the mere presence of a highly toxic hydrocarbon like benzene can make water unsafe to drink (Maurice *et al*., 2019; Zhou *et al*., 2021). Studies have shown that water pollution remains one of the major environmental public health problems arising from extensive oil operations in the region, leading to several cases of water-borne illness annually (Ana, 2011; Nwilo and Badejo 2005; Bodo and David, 2018; Bodo and Gimah, 2019). The concentration of polycyclic aromatic hydrocarbons (PAHs) in surface water in the Niger Delta was found to be higher than the recommended limits for drinking water, with toxic PAHs being prominent near the point source, making the consumption of aquatic habitats from these creeks unsafe (Nwineewii and Marcus, 2015).

Therefore, understanding the level of petroleum hydrocarbon contamination in surface water is crucial to protect the environment and human health. Previous studies have demonstrated that crude oil pollution can negatively impact the physicochemical properties of water systems. For instance, Ogbonna *et al*; (2021) observed adverse effects of crude oil pollution on surface water around Bodo/Bonny coastal waters, while Onwuna *et al*; (2022) found that water around Igia-Ama, Tombia, in Rivers State was affected by the illegal disposal of crude oil refined waste products. Furthermore, the presence of total petroleum hydrocarbons (TPH) and heavy metals such as Cadmium (Cd), Lead (Pb), and Nickel (Ni) has been implicated in surface water systems following crude oil spills (Okon *et al*., 2021; Ejairu and Okiotor, 2022). In such incidents, crude oil compounds can dissolve and diffuse into sediments, disrupting natural systems and potentially leading to ecological and health effects (Ordinioha and Brisibe, 2013; Odisu *et al*., 2021; Orisakwe, 2021).

Given the consistent occurrence of crude oil spills in rivers and creeks in the Niger Delta and the associated risks, it is essential to determine the concentration levels of components of crude oil and implement measures for mitigation, remediation, and ongoing post-impact assessments to ensure that remediation efforts are effective (Nkeeh *et al*., 2021; Choudhury *et al*., 2021). As such, the aim of this study is to determine the total petroleum hydrocarbon levels in surface water at Effurun Roundabout in Warri, Delta-State, with implications for environmental and human health. Effurun Roundabout, located in Warri, Delta State, Nigeria, is a significant transportation hub where heavy vehicular traffic occurs. The study area is also close to several oil refineries and petrochemical plants. These factors increase the likelihood of petroleum hydrocarbon contamination in surface water.

Materials and Methods

Study Area

Effurun Roundabout serves as an entry and exit point for the city of Warri, and is located in the Uvwie Local Government Area of Delta State, Nigeria. The roundabout is situated near the Nigerian National Petroleum Corporation (NNPC) right of way, which carries crude oil. An oil spillage and petroleum-induced fire occurred in the area on Friday 4th of December, 2015, two weeks after an earlier and similar accident, resulting in pollution at four different sampling points in the area (Premium Times Nigeria, 2015). The study area is a periodical wetland that receives water from surrounding areas during the rainy season and dries up during the dry season, with the roundabout and right of way being part of it. The area is used by people around the area for farming during the dry season. The area is also characterized by a low water table and loamy soils, which makes it highly vulnerable to TPH contamination in the occurrence of a spill incident. The right of way around the roundabout makes the area susceptible to pollution from oil spills and leaks potentially damaging the ecosystem in the long run. Digital global positioning system (GPS) coordinates were used to locate and label each of the five sampling points (A, B, C, D, and E) accurately. These points were collected and labelled in the field using representation A (N5°34′27″, E5°46′52″), B (N5°34′32.9″, E5°46′57.9″), C (N5°34′33.5″, E5°46′56.2″), D (N5°^{0}34′33.9″, E5°46′54.7″), and E (N5°34′12″, E5°50′27″), with sample E serving as the control. Figure 1 is a map that shows the buffered section of the sites where samples were collected from.

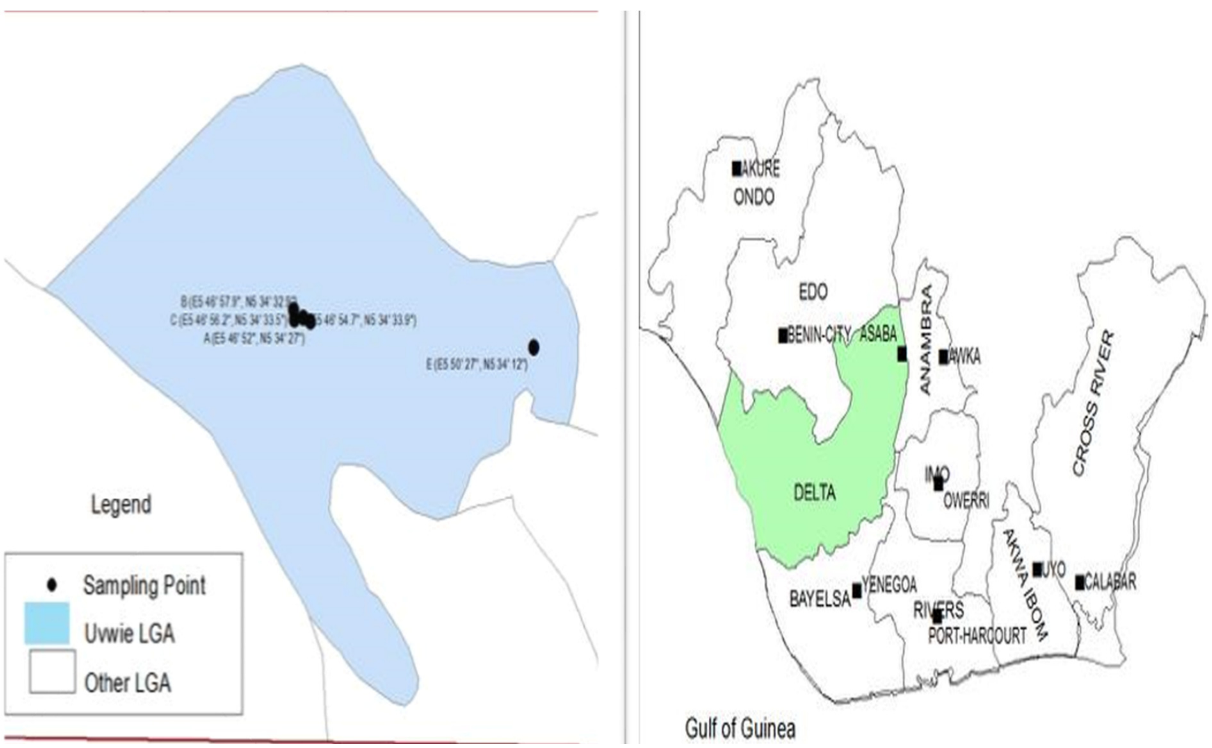

Fig. 1: Map of the Study area showing sample locations

Sample Collection

Sampling was done during the rainy season, precisely in June 2016. Standard sampling protocol was developed from USEPA (2007), sampling design for surface water sampling procedure. Four water samples were collected from different locations at Effurun roundabout where pipeline leakage had caused spills, and a control sample was collected from the Federal University of Petroleum Resources, Effurun, which was over 100m from the study area. The samples were collected using glass jar containers and amber bottles to avoid contamination. To prevent the samples from reacting with plastic containers, wide-mouth 500 ml glass bottles with Aluminium foil were tightly fitted for polycyclic hydrocarbon analysis. The samples were labelled and stored in cold boxes before being taken for analysis. The glass bottles used for sample collection were cleaned and dried before use to avoid contamination. On-site filtration and preservation with concentrated Tetraoxosulphate (VI) acid (conc. H_2SO_4) prevented microbial growth and ensured sample stability during transportation. The samples were labelled, stored in a temperature medium of ≤ 4°C, and transported to the laboratory for analysis.

Sample Preparation and Extraction

The extraction procedure of the collected water sample was carried out following US EPA method 3510C (US EPA, 1996), where 40 ml of acetone-n-hexane was mixed with 100 ml of the water sample. A litre of the water sample was subjected to liquid-liquid extraction in a separatory funnel using 50 ml of dichloromethane (DCM) as the extracting solvent. The organic layer was collected and concentrated using anhydrous sodium sulphate and a rotary evaporator. Two columns were prepared for each sample, one for Aliphatic Hydrocarbon and the other for Aromatic Hydrocarbon.

The water extracts were transferred into chromatographic columns packed with pre-conditioned silica gel and cleaned using dichloromethane for aromatic hydrocarbon while using n-hexane for aliphatic hydrocarbon. The spiked sample was treated similarly to the main sample for quality assurance and added to a vial bottle subjected to GC analysis (Maioli *et al*; 2011). Gas chromatography analysis was conducted using a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector. The gas chromatograph was calibrated using petroleum hydrocarbon calibration working standards prepared in the range of 0.05–20 mg/mL using n-hexane as diluent. TPH was quantified by integrating the baseline holding and peak sum slicing and then quantifying as the sum of concentrations of the n-alkanes that eluted from nC–8 to nC–40 and unresolved complex mixture (UCM). Data analysis was carried out using the Agilent software, from which the low molecular n-alkanes/high molecular n-alkanes and unresolved n-alkanes/resolved n-alkanes were obtained (Luan and Szelewski, 2008; Cortes *et al*., 2012).

Statistical Analysis

The study involved triplicates for all determinations and the results were presented as mean ± standard deviation. Correlations between hydrocarbon components was conducted using IBM SPSS statistics 25.

Results and Discussion

Analysis of n-Alkane Distribution in Surface Water Contaminated with Crude Oil at Effurun Roundabout, Delta State

The present study focused on analysing the distribution of n-alkanes in surface water contaminated with crude oil at Effurun roundabout, Delta State. The analysis was conducted on four samples, namely A, B, C, and D, and the results are presented in Table 2. The study found that the Alkanes nC8, nC36, nC18, nC17, and nC10 had the highest concentrations in all the samples, as shown in table 2. Additionally, Pristane and Phytane, the isoprenoid hydrocarbons, were detected in all the samples.

Based on the classification provided by Kuppusamy *et al*. (2020), Sample A, showed contamination with hydrocarbons in the gasoline range organics (GRO) and oil range organics (ORO) categories, indicating the breakdown of longer chain hydrocarbons due to environmental conditions. Hydrocarbons within the carbon range of nC23 and nC27 were not detected in this sample. Sample B had hydrocarbons within the carbon range of nC8 to nC40, except for C9 and C13. C21 and C32 had the highest concentration range in Sample B, with concentrations of 1.30063mg/L and 1.16238mg/L, respectively. Sample C showed the highest concentration range of hydrocarbons in C11, C12, and C17, with concentrations of 1.99805mg/L, 5.19997mg/L, and 1.01428mg/L, respectively. In Sample C, C9 was the only hydrocarbon that was not detected. Sample D had all hydrocarbons detected, except for C12. The high concentration of alkane compound in Sample C could be attributed to the fact that the pipeline leakage started from this location. On the other hand, Samples B and D had the lowest concentration of alkane compounds, possibly due to the crude oil spill from location C being washed down the river by environmental conditions such as topography and river flow. Overall, the study findings underscore the importance of monitoring surface water quality in areas affected by crude oil contamination.

The results showed that the alkanes nC8, nC36, nC18, nC17, and nC10 had the highest concentrations in all the samples, which is consistent with findings from other studies on crude oil contamination. In the study conducted by Odisu *et al*; (2021) in the Niger Delta region of Nigeria reported higher concentrations at below surface water levels in oil-contaminated water samples. Results of alkane analysis were also found to be higher in this study from results from the west coast of Korea that was polluted by a crude oil tanker that spilled on the river (Kim *et al*., 2013). In addition, the detection of Pristane and Phytane, the isoprenoid hydrocarbons, in all the samples is also consistent with previous research. For instance, a study by Iheonye *et al*. (2019) in the Sombreiro River in Akuku-Toru Local Government Area Rivers State, Nigeria reported the presence of Pristane and Phytane in crude oil-contaminated water samples.

Table 2: Results of the Aliphatic Hydrocarbon Content

Component	Sample A [mg/L]	Sample B [mg/L]	Sample C [mg/L]	Sample D [mg/L]	Control [mg/L]
C8	1.33095	6.34E-01	4.15E-01	2.24E-01	2.61E-02
C9	8.11E-02	Nd	Nd	4.17E-01	2.64E-02
C10	7.10E-01	4.02E-01	4.57E-01	4.00E-01	1.83E-02
C11	2.42E-01	2.49E-01	1.99805	3.62E-01	5.83E-02
C12	6.35E-01	1.22E-01	5.19997	Nd	9.47E-02
C13	4.25E-01	Nd	3.07E-01	3.17E-01	5.72E-02
C14	4.26E-01	3.16E-01	6.48E-01	4.61E-01	6.06E-02
C15	5.61E-01	4.26E-01	8.08E-01	3.77E-01	6.23E-02
C16	3.53E-01	1.72E-01	6.57E-01	3.96E-01	5.78E-02
C17	8.39E-01	1.10E-01	1.01428	6.38E-01	5.14E-02
Pristane	6.43E-01	1.80E-01	5.46E-01	8.81E-01	4.05E-02
C18	1.02544	6.25E-01	4.96E-01	2.27E-01	5.83E-02
Phytane	2.28E-01	2.40E-01	3.27E-01	4.31E-01	4.36E-02
C19	3.80E-01	4.58E-01	2.68E-01	2.70E-01	4.31E-02
C20	4.64E-01	6.63E-01	2.50E-01	1.06E-01	5.41E-02
C21	1.37E-02	1.30063	7.92E-01	9.50E-01	5.23E-02
C22	2.31E-01	4.77E-01	4.89E-01	6.98E-01	5.25E-02
C23	Nd	9.92E-01	4.40E-01	6.32E-01	3.48E-02
C24	2.02E-01	3.40E-01	2.76E-01	3.15E-01	5.23E-02
C25	3.02E-01	1.37E-01	3.08E-01	1.79E-01	5.92E-02
C26	3.16E-01	2.98E-01	1.89E-01	6.19E-01	8.42E-02
C27	Nd	1.10E-03	1.28E-01	5.07E-01	5.90E-02
C28	2.39E-01	2.50E-01	3.21E-01	2.67E-01	7.01E-02
C29	3.89E-01	4.15E-01	3.55E-01	1.73E-01	1.27E-02
C30	4.61E-01	1.45E-01	2.34E-01	1.96E-01	9.87E-02
C31	1.77E-01	9.20E-01	9.29E-01	1.07E-01	8.65E-02
C32	5.62E-01	1.16238	7.16E-01	6.31E-01	9.40E-02
C33	2.12E-01	5.84E-01	5.62E-01	4.31E-01	7.19E-02
C34	3.78E-01	8.26E-01	2.39E-01	2.94E-01	5.41E-02
C35	2.22E-01	8.25E-01	1.32E-01	1.09E-01	3.93E-02
C36	1.02632	5.71E-01	4.44E-01	4.02E-01	4.22E-02
C37	6.15E-01	3.41E-01	3.07E-01	3.93E-01	Nd
C38	3.99E-01	1.93E-01	2.85E-01	2.40E-01	Nd
C39	5.77E-01	1.29E-01	5.21E-01	4.00E-01	Nd
C40	3.72E-01	3.41E-01	4.17E-01	8.44E-01	Nd
TOTAL	14.28165	14.8478	19.92783	13.89272	1.71647

*ND; not detected

Assessment of Polyaromatic Hydrocarbon (PAH) Contamination in Water Samples from Effurun Roundabout

Table 3 shows the concentrations of polyaromatic hydrocarbons (PAH) in water samples collected from the Effurun roundabout. The concentrations of PAH compounds in the samples varied widely. In sample A, Anthracene and Benzo (b) fluoranthene were the major PAH compounds, with concentrations of 1.72218mg/L and 1.21579mg/L, respectively. In sample B, Acenaphthene had the highest PAH concentration, with a concentration of 2.04217mg/L. Benzo(a)anthracene and Fluoranthene were not detected in sample B. Sample C had detectable levels of Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Indeno(1,2,3-cd)pyrene, 2-Methylnaphthalene, Phenanthrene, and Pyrene with concentrations of 1.61861mg/L, 1.32808mg/L, 1.30177mg/L, 1.01697mg/L, 1.37298mg/L, and 1.12610mg/L, respectively.

Table 3: PAH Concentration in surface water samples collected

Component	Sample A [mg/L]	Sample B [mg/L]	Sample C [mg/L]	Sample D [mg/L]	Control [mg/L]
Acenaphthene	9.02913E-1	2.04217	1.42500E-1	4.48920E-1	-
Acenapthylene	2.97087E-1	7.69977E-1	3.74011E-1	8.50643E-1	-
Anthracene	1.72218	1.11319E-1	-	1.39254E-1	-
Benzo(a)anthracene	8.32826E-1	-	3.15682E-1	8.85468E-1	3.33128E-2
Benzo(a)pyrene	5.05787E-1	1.63709E-1	3.40318E-1	2.74221E-1	-
Benzo(b)fluoranthene	1.21579	3.54639E-1	3.77244E-1	1.91997E-1	-
Benzo(g,h,i)perylene	9.18689E-1	7.64614E-1	1.61861	1.21464E-1	-
Benzo(k)fluoranthene	4.93054E-1	2.79866E-1	1.32808	1.19314E-1	-
Chrysene	1.09550E-1	1.21161E-1	9.70297E-3	8.41952E-1	3.56618E-2
Dibenz(a,h)anthracene	6.38316E-3	8.24756E-2	3.35758E-1	2.53163E-1	-
Fluoranthene	216649E-2	-	5.53358E-1	6.72716E-2	2.66909E-2
Fluorene	2.24134E-1	6.77188E-1	6.99122E-1	1.91171E-1	9.16318E-2
Indeno(1,2,3-cd)pyrene	2.56017E-1	1.68424E-1	1.30177	9.13696E-2	-
2-Methylnaphthalene	3.56688E-1	2.72154E-1	1.01697	4.77571E-1	8.73079E-2
Naphthalene	3.53607E-1	6.17915E-1	1.53017E-1	1.00750	-
Phenanthrene	1.57414E-1	1.32727E-1	1.37298	3.68012E-1	2.70239E-2
Pyrene	1.81219E-1	2.63863E-1	1.12610	6.87309E-1	4.69566E-2
TOTAL	8.55500	6.82220	11.06523	6.89127	0.348586

The high PAH levels found in the current study are thought to be petrogenic in origin due to similar molecular weights. The contamination of surface water by petroleum may be linked to the high PAH levels observed in the samples, and there is a possibility of the groundwater aquifer becoming contaminated by constituent pollutants seeping proximally. The maximum permissible limit for total PAHs in drinking water, as recommended by the World Health Organization, is 0.0002mg/L (Ekere *et al*; 2019). The concentrations of PAHs in the water samples exceeded this limit, and this raises public health concerns as some PAHs have been confirmed to be carcinogenic. PAH concentration from this study was found to be higher than results obtained from crude oil polluted groundwater at Okrika mainland in Imo state, Nigeria (Ogbuagu *et al*., 2011).

Comparison of Chemical Composition in Samples from a Pollution Site and Control: Aliphatic, PAH and PHC Concentrations and Ratios

As shown in Table 4 below, the sample with the highest petroleum hydrocarbon (PHC) concentration was observed to be sample C which has a concentration of

30.99306mg/L. this was collected at the Effurun round-about. This high PHC concentration can be attributed to the fact that the pipeline leakage started very close to the location where sample C was collected. Sample A has a PHC concentration of 22.83665mg/L. it is slightly higher than sample B with a PHC concentration of 21.67000mg/L. Sample A is, therefore, the location with the second highest PHC concentration. This high PHC concentration can be attributed to the fact that mechanic workshops close to the points of impact.

Table 4: Result of the composition of Aromatic and Aliphatic Fractions

Component	Sample A	Sample B	Sample C	Sample D	Mean around pollution site (± SD)	Control
Aliphatic (mg/L)	14.28165	14.8478	19.92783	13.89272	16.910±3.018	1.71647
PAH (mg/L)	8.555	6.8222	11.06523	6.89127	8.944±2.122	0.348586
PHC (mg/L)	22.83665	21.67	30.99306	20.78399	25.885±5.105	2.065056
Aliphatic/PHC (%)	62.538	68.518	64.298	66.8433	65.528±2.99	83.12
PAH/PHC (%)	37.462	31.482	35.702	30.157	33.810±3.653	16.88

The mean concentrations of pollutants around the pollution site are much higher than those in the control sample, indicating that there is a significant pollution problem in the area. The standard deviations for the mean concentrations suggest that there is some variability in the level of pollution around the site. The ratio of aliphatic to PHC in the samples ranges from 62.538% to 68.518%, with a mean of 65.528% ± 2.99%, indicating that aliphatic compounds are the dominant type of pollutant in the samples. The ratio of PAH to PHC ranges from 30.157% to 37.462%, with a mean of 33.810% ± 3.653%, suggesting that PAHs also contribute significantly to the pollution in the area.

Identifying Significant Contributors using Correlation Analysis

The graph shown in figure 2 below shows the correlation curves between aliphatic hydrocarbon and petroleum hydrocarbons. The correlation curve between aliphatic hydrocarbon (Aliphatic HC) and petroleum hydrocarbon (PHC) concentrations in the four surface water samples polluted with crude oil shows a positive correlation between the two variables. The values of Aliphatic HC and PHC increase in each sample, indicating that both pollutants are present and that their concentrations are positively related.

In sample C, the Aliphatic HC and PHC values were 20 and 31, respectively, which is higher than the values in the other samples. This suggests that sample C may have been contaminated with crude oil that contains a higher proportion of aliphatic hydrocarbons relative to other hydrocarbon types, such as aromatics or polycyclic aromatic hydrocarbons (PAHs).

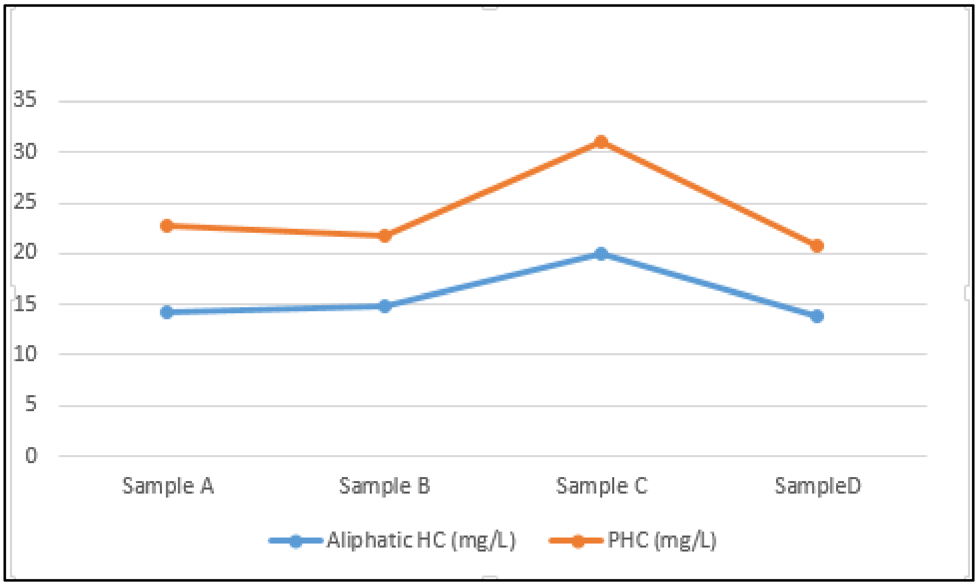

Fig. 2: Correlation Curves between Aliphatic Hydrocarbon and PHC

In contrast, the values of Aliphatic hydrocarbons (HC) and PHC in sample D were lower than those in the other samples, indicating that this sample may have been contaminated with a crude oil that contains a higher proportion of other types of hydrocarbons, such as PAHs, relative to aliphatic hydrocarbons. The positive correlation between Aliphatic HC and PHC concentrations in the surface water samples suggests that the two pollutants have similar sources and transport mechanisms, and that the concentrations of one pollutant can be used as a proxy for the concentrations of the other pollutant. However, the variation in the Aliphatic HC and PHC values across the different samples highlights the importance of monitoring the concentrations of different types of hydrocarbons in crude oil-contaminated surface water to accurately assess the degree of contamination and potential risks to human and environmental health.

The graph shown in figure 3 displays the correlation curves between polyaromatic hydrocarbon (PAH) and petroleum hydrocarbon concentrations. The correlation curve between polyaromatic hydrocarbon (PAH) and petroleum hydrocarbon (PHC) concentrations in the four surface water samples polluted with crude oil shows a positive correlation between the two variables. The values of PAH and PHC increase in each sample, indicating that both pollutants are present and that their concentrations are positively related.

In sample B, the PAH and PHC values were 7 and 22, respectively, which is lower than the values in sample C, where the PAH and PHC values were 11.5 and 31, respectively. This difference in values may be due to the different sources and ages of the crude oil present in each sample, as well as the environmental conditions in which the samples were collected. Sample C may have been contaminated with a more weathered crude oil, which would contain a higher proportion of PAHs relative to PHCs.

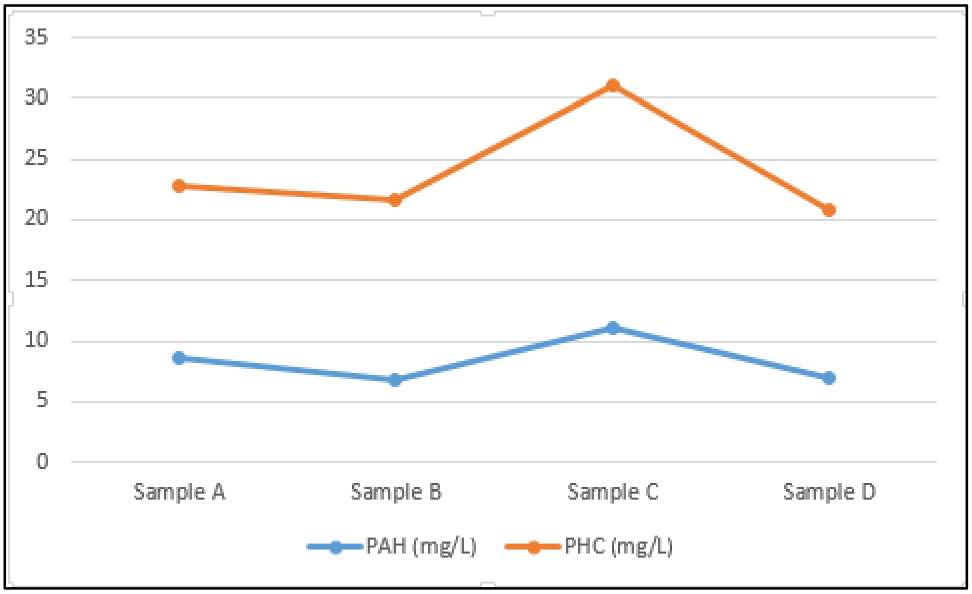

Fig. 3: Correlation Curves between PAH and PHC

The PAH and PHC values in sample A and sample D were also lower than those in sample C, which suggests that the degree of contamination with crude oil and the corresponding concentrations of PAH and PHC are not uniform across the contaminated site. Overall, the positive correlation between PAH and PHC concentrations in the surface water samples indicates that the two pollutants have similar sources and transport mechanisms and that the concentrations of one pollutant can be used as a proxy for the concentrations of the other pollutant.

The correlation curve between Aliphatic HC and PAH shown in figure 4 concentrations in the four surface water samples polluted with crude oil shows a weak positive correlation between the two variables. The values of Aliphatic HC and PAH increase in each sample, but the overall values are relatively low.

In samples A, B, and C, the values of Aliphatic HC are consistently higher than those of PAH, indicating that the crude oil in these samples may contain a higher proportion of aliphatic hydrocarbons compared to PAHs. However, in sample D, the value of Aliphatic HC is much lower than that of PAH, suggesting that this sample may be contaminated with a crude oil that contains a higher proportion of PAHs relative to aliphatic hydrocarbons.

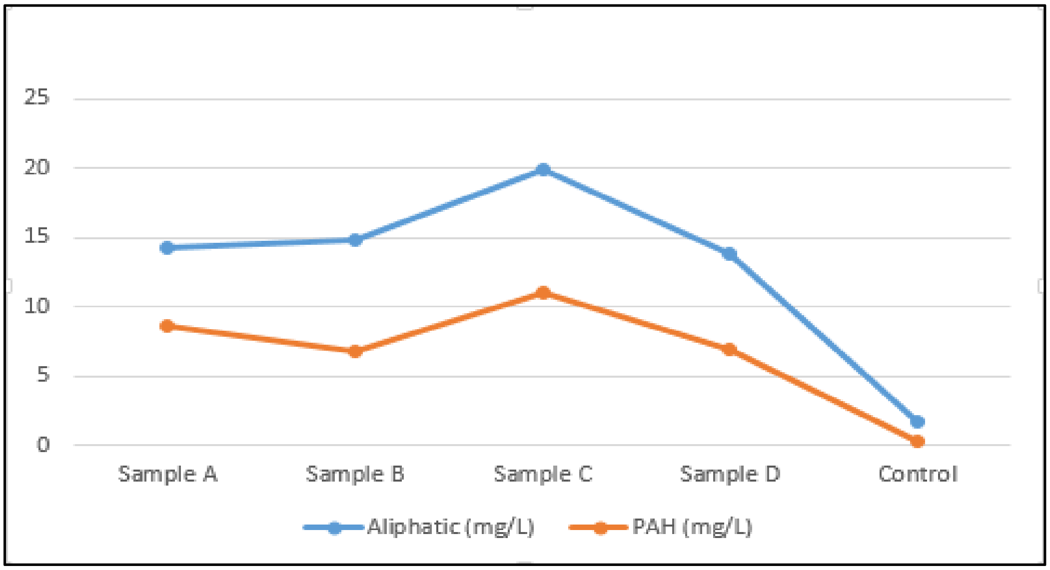

Fig. 4: Correlation Curves between PAH and Aliphatic HC (mg/L)

Overall, the weak positive correlation between Aliphatic HC and PAH concentrations in the surface water samples suggests that the two pollutants may have different sources and transport mechanisms. While both pollutants are commonly found in crude oil, their concentrations may vary depending on the specific source of the oil and the environmental conditions that the oil has been exposed to.

It is important to note that the concentrations of both Aliphatic HC and PAH are relatively low in all four samples, which may indicate that the crude oil pollution is not significant or has not persisted in the surface water for a long time. However, further monitoring and analysis may be needed to fully understand the extent and potential risks of the contamination to human and environmental health.

As shown in table 5, Pearson product correlation of aliphatic hydrocarbons and PAH was found to be strongly correlated and statistically significant (r = 1.000, $p<0.01$). This goes on to show that in the sampled sites an increase in the concentration of polyaromatic compounds will lead to an increase also in the concentrations of aliphatic compounds in the surface water.

Table 5: Correlation Analysis

Correlations			
		Aliphatic	PAH
Aliphatic	Pearson Correlation	1	1.000**
	Sig. (2-tailed)		.000
	N	35	17
PAH	Pearson Correlation	1.000**	1
	Sig. (2-tailed)	.000	
	N	17	17

**. Correlation is significant at the 0.01 level (2-tailed)

Conclusion

In conclusion, the results of this study suggest that crude oil contamination of surface water poses a significant threat to public health and the environment. The presence of n-alkanes and polyaromatic hydrocarbons (PAHs) in surface water contaminated with crude oil can cause respiratory problems, skin irritation, and even cancer. The concentration of some PAH compounds in all sampling sites was above the threshold limits for International and State Regulatory Agencies. Furthermore, the concentration of PAH in the water samples was higher than the permissible limit set by the World Health Organization, which raises public health concerns. These findings suggest that the study area is under pollution threat, and the need for early remediation measures is necessary as the cleanup done previously after the spill was insufficient to restore the integrity of the environment.

It is essential to monitor surface water quality in areas affected by crude oil contamination to prevent public health hazards. The Total Petroleum Hydrocarbon (TPH) concentration of water samples in surface water at the study area indicated that all sites had significant levels of Aliphatic Hydrocarbons than Polycyclic Aromatic Hydrocarbons. The sample C site, which is close to where the pipeline leakage occurred, had the highest TPH concentration than other sample sites.

The findings of this study highlight the need for continued monitoring of surface water quality in areas affected by crude oil contamination. Efforts should be made to prevent and minimize the contamination of surface water to protect public health. It is also imperative that remediation measures are taken promptly to restore the integrity of the environment. Future studies should be conducted to determine the extent of groundwater contamination and its potential impact on public health. This study provides valuable information that can be used to develop strategies and policies to prevent the contamination of surface water by crude oil and mitigate its adverse impacts on human health and the environment.

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