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ORIGINAL RESEARCH ARTICLE

ASSESSMENT OF PAHs IN BOREHOLE WATER FROM THE VICINITY OF THE DELTA STEEL COMPANY, WARRI, DELTA STATE, NIGERIA

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ABSTRACT

Water contamination due to industrialization is a major problem affecting the environment and all life. This work evaluates the existence of polycyclic aromatic hydrocarbons (PAH) in borehole water from Delta Steel Company in Warri, Delta State. The water sample was analysed in accordance with the US Environmental Protection Agency (EPA) using a gas chromatography-mass spectrometer (GC-MS). The concentration of Σ16 PAH in water from the sampling site shows that the concentration was in the range of 23.78 – 125.9 mg/L. The study further shows that groundwater in the area was polluted with both light and heavy PAH concentrations. The light PAH concentrations were about 43.8%, ranging from 26.4 mg/L and 50.04 mg/L. Whereas the heavy PAH concentrations were about 56.2%, ranging from 23.78 mg/L and 125.9 mg/L, with Benzo (a) pyrene at 0.0001 mg/L and 0.002 mg/L for all other PAHs that exceed the World Health Organization permissible limit of 0.002 mg/L. Heavy PAHs were dominant, with benzo(a)fluoranthene accounting for the highest concentration in the samples. The four- five- ring PAHs were the dominant group of PAHs in the study. This observation was attributed to the prolonged industrial practices in the area. Therefore, this study recommends that, for health and safety, the water be subjected to major treatment before consumption.

1.0 Introduction

Environmental pollution has long been a topic of discussion globally as a result of its impact on humans and the environment (Wang *et al*., 2019). This is because, as a result of urbanization and industrialization, there has been an increase in the exploration and exploitation of natural resources, which has resulted in the release of several organic pollutants such as polycyclic aromatic hydrocarbons (PAHs), which are found in coal, wood, gasoline, volcanic activities, and the burning of wastes in the environment (Halek, et al., 2006; Maliszewska-Kordybach, et al., 2009) (Mojiri *et al*., 2019) (Shariatifar, et al., 2021) (Roudbari, et al., 2021). In addition to being released into the atmosphere by incomplete burning of crude oil, wood, coal gas, and other organic substances, which are globally widespread and present in various ecosystems, PAH pollutants are a problem (Masih *et al*., 2008) (Okoli *et al*., 2011, Grand-clement *et al*., 2017, Adeniji *et al*., 2019).

Abolfazi and Elahe (2008), Vidal et al. (2011), and Karyab et al. (2013) highlighted that harmful substances from road run-off, oil spills, and leaching from creosote-impregnated wood typically cause water sources to become contaminated. Other authors (Wakeham, et al., 1980; Hostettler, et al., 1999; Chimezie & C, 2006; Adekunle, et al., 2017; Okedere & Elehinafe, 2022) have reported the pollution of PAHs in wastewater, seawater, surface water and ground water.

Furthermore, PAHs are believed to be endocrine disruptive compounds (ED) capable of suppressing the immune system, and human exposure to PAHs has been related to a number of disorders including cancer, heart disease, and asthma (Londono, et al., 2015; Sharifiarab, et al., 2022).

According to Vishi et al. (2005), PAHs are aromatic hydrocarbons that include two or more benzene rings in various structural configurations. Heavy PAHs are defined as having more than four rings and are more stable than light PAHs, according to Li et al. (2016). Light PAHs, on the other hand, are those with three rings or fewer. Studies (Purcaro, et al., 2013; Duedahl-Olesen, et al., 2015), have shown that there are over a hundred of these (PAHs) in nature. However, 16 of them have been suggested as priorities by the US Environmental Protection Agency (US EPA) for monitoring in food and environmental matrices due to their toxicity and prevalence (Ergonul & Sanchez, 2013; Iwegbue, et al., 2021).

The prevalent discovery of PAHs in sources of water like saltwater, groundwater, and river water is due to rising human activity as well as inappropriate and unregulated waste disposal. Furthermore, due to the high levels of PAH, many of these water sources have been deemed dangerous for human consumption (Lee & Shin, 2010). This has led to the shortage of portable water which is generally a global problem (Wang, et al., 2019)

In most coastal settlements, underground water pumped from aquifers provides the main source of fresh water for both drinking and other household uses, especially in DSC, Warri in Delta state. This source of water is prone to contamination by PAHs, which can migrate a long distance from their point of emission (Iwegbue, et al., 2021). Recent complaints of perfumed and crude oil-tainted water, as well as residents' observations of crude oil films on the top of water taken from public boreholes, served as the basis for this study. Nonetheless, there has been no study of PAH on these boreholes to date, which makes it important in terms of health consideration, given the proximity of the residence to the steel company. Determining the PAH concentration in borehole water obtained from DSC in Warri, Delta State, Nigeria, is the goal of this study.

2. Materials and Methods

2.1 Description of study area

The research area in DSC, Warri, Delta State, which is situated in the oil region of southern Nigeria, is seen in Figure 1. It shares boundaries with Sapele, Udu and Uwvie. The latitude and longitude of Warri are at 5.544230, 5.760269 respectively. It has residents of over 311,970 people (NPC, 2006). Hence, the large population and commercialization especially due to petroleum activities in the study area makes it possible for the alteration of the natural constituent of the natural environment. The locations, source, and coordinates of the water samples that were obtained in DSC, Warri, are displayed in Table 1.

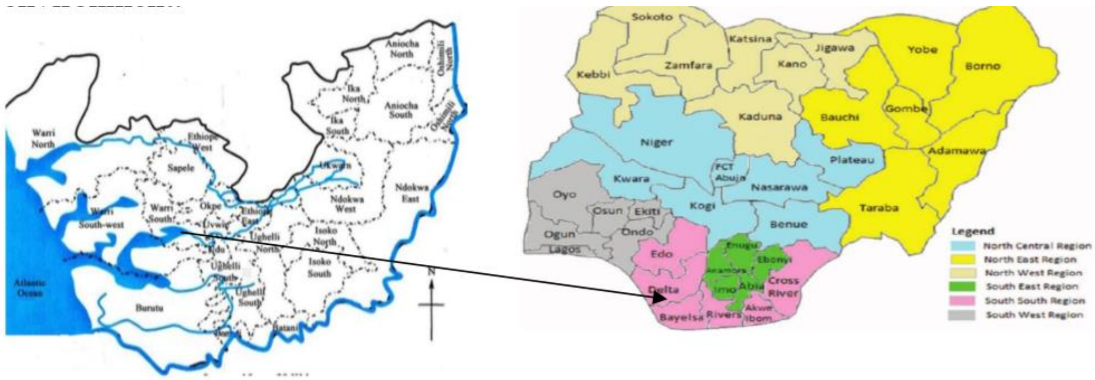

Figure 1: The sampling area is depicted on a map of Nigeria that includes Warri, Delta state (Esinulo, et al., 2016).

Table 1: Description of Water Samples Collected from DSC Metropolis

Sample location	Source	Longitude	latitude
Ekete waterside	Borehole	5.492909	5.821895
Ekete waterside	Borehole	5.495130	5.818762
Ekete waterside	Borehole	5.495386	5.814213
Ekete waterside	Borehole	5.500314	5.810617
Ekete waterside	Borehole	5.505750	5.825264
Igbogidi	Borehole	5.510931	5.823070
Ekete waterside	Borehole	5.511643	5.834042
Ekete waterside	Borehole	5.501483	5.835471
Ekete inland	Borehole	5.495082	5.793469
Ekete inland	Borehole	5.493253	5.795970
Ekete inland	Borehole	5.496860	5.799696
Ekete waterside	Borehole	5.495031	5.807402
DSC High Asagba	Borehole	5.618943	7.167605
DSC High	Borehole	5.619943	7.166605

2.2 Sample Collection

14 boreholes at DSC, Warri, Delta State, Nigeria were used to collect a total of 42 water samples (in triplicate). 1L brown glass bottles with no air bubbles were used to collect the samples. The bottles were thoroughly washed before the samples were collected for analysis to prevent contamination.

2.3 Extraction of PAHs from Samples

For the analysis of semi- and non-volatile organics, the United States Environmental Protection Agency (USEPA) Method 3510 for aqueous matrix was utilized (USEPA, 2016). After filtration, a 100mg/L sample water was put in a 2L glass separation funnel. 30mg/L of the saturated sodium chloride (NaCl) was then added and thoroughly mixed. 100mg/L of dichloromethane (CH_2Cl_2) was then added as an extraction solvent and properly mixed. The mixed sample was given a few minutes to settle before the dichloromethane (CH_2Cl_2) extract was taken. The organic layer was placed over anhydrous magnesium sulphate and dried together after the extraction procedure was repeated with 100mL of dichloromethane. After being concentrated using a 2mL rotary vacuum evaporator, the sample extract was cleaned up.

2.4 PAH evaluation Using GC-MS

After being carefully packed in a 10 mL polypropylene cartridge column and activating 1g of silica gel at 130 ^{O}C for 10 hours, the cartridge was conditioned with 6 mL of dichloromethane (CH_2Cl_2). A column was loaded with the concentrated cartridge, and the extract was collected using a pear-shaped flask that was positioned underneath the column. Following rotary evaporator drying of the entire filtrate concentration at 38 °C, the column was eluted with 10mg/L dichloromethane (CH_2Cl_2). The residue was next diluted in 1 mL of methanol and placed in a 2 mL standard vial before being quantified using a GC while helium was flowing at a rate of 1.4 mL/min.

2.5 Statistical Analysis

Experimental data obtained were analysed using Microsoft Excel 360 to evaluate the mean standard deviation and percentage.

3. Results and Discussion

Table 1 displays the findings of the water samples tested by DSC, Warri, for PAH content. The presence of all 16 PAHs in varying quantities in the water samples drawn from the borehole attests to how prevalent the contaminants are (Wang, et al., 2018). Since there is currently no limit in place for Nigeria, this study was conducted using WHO guidelines (Onydinma, et al., 2021).

The concentrations of all samples, regardless of the sampling point, were generally above the WHO permissible limit. The highest mean result from the sample site was Benzo(b)fluoranthene at 125.9 mg/L, followed by Indeno(1,2,3-cd)pryene at 96.76 mg/L. Given that fossil fuels have been shown to be present in rainwater, these contaminants may have originated there (WHO, 1998; Kim, et al., 2011). Benzo(g,h,i)pyrene and benzo(k)fluoranthene were among those that also displayed high mean values, with 74.68 and 91.44 mg/L, respectively. According to Pan et al. (2005), Benzo(k)Fluoranthene is a harmful contaminant that is apparently becoming more prevalent in water sources.

Anthracene and benzo(g,h,i)pyrene had mean values of 24.22 and 26.4mg/L, respectively, whereas Chrysene had the lowest mean value at a mean concentration of 23.78 mg/L. Studies have shown that chrysene is one of the most insistent PAHs in water linked to improper fuel combustion and is difficult to remove (Wang, et al., 2013; Dimante, et al., 2017).

From the results, the greatest mean value was for the 5R PAH homologue, which was followed by the 6R homologue with values of 51.55 and 32.75 respectively. Whereas, 4R homologue had the lowest mean value at 25.33. There was a 0.12 to 0.63ppm variation in the mean PAH content. This contrasts with Wang et al.'s works from 2021, which had a PAH content of 0.0003ppm.

Table 1. Concentrations of PAHs from borehole water sample

Name	Amount ppm	Concentration (mg/L)	WHO Permissible limit (mg/L)
Napthalene	0.15	29.3	0.002
Acenapthylene	0.24	47.94	0.002
Acenapthene	0.25	50.04	0.002
Phenanthrene	0.18	36.64	0.002
Fluorene	0.16	31.7	0.002
Fluoranthene	0.23	45.32	0.002
Anthracene	0.13	26.4	0.002
Pyrene	0.27	53.1	0.002
Benz (a) anthracene	0.14	27.08	0.002
Chrysene	0.12	23.78	0.002
Benzo (k) fluoroanthene	0.46	91.44	0.002
Benzo (b) fluoranthene	0.63	125.9	0.002
Indeno (1,2,3-cd) pyrene	0.48	96.76	0.002
Benzo(a)pyrene	0.17	34.3	0.0001
Dibenz (a,h) anthracene	0.37	74.76	0.002
Benzo (g,h,i) perylene	0.12	24.22	0.002

Table 2 shows the different PAH homologues present in the water sample analyzed from the borehole in DSC Warri. The result shows 16 PAH were observed to be present in the 2-, 3-, 4-, 5-, and 6-ring homologues. The 2-ring PAH (Napthalene, acenapthylene, and acenapthene) was detected to be 15.6% in the water sample at varying concentrations between 29.3 and 50.04mg/L. Poor handling of petroleum products may be related to the presence of naphthalene. It is one of the oil spill-derived petrogenic PAHs with a low molecular weight (Sun, et al., 2016). The 3-ring PAHs Fluorene, anthracene, phenanthrene, which is regarded as a tracer for vehicular emissions (Sun, et al., 2016), and fluoranthene were detected to be 17.11% in the water sample at varying concentrations of 26.4 and 36.64mg/L. The 4-ring PAH (pyrene, Benz(a)anthracene, and chrysene) was detected to be 10.9% in the water sample, with varying concentrations between 2.90 and 6.49mg/L. The 5-ring PAHs Benzo(a)pyrene), (Benzo(k)fluoranthene, Benz(b)fluoranthene, and dibenz(a,h)anthracene were detected to be 42.96% in the water sample, with varying concentrations between 34.3 and 125.9mg/L. The 6-ring PAH (Benzo(g,h,i)pyrene, Indeno(1,2,3-cd)pyrene) was detected to be 12.09% in the water sample, with varying concentrations between 24.22 and 96.76mg/L.

It was found that the PAH concentrations were higher than those found in the studies of Badawy & Enababy (2010). However, the percentage distribution of PAH 43.8% belongs to 2- and 3-ring PAHs (Figure 2). This is an indication that 56.2% are heavy PAHs which are steadier and are extra toxic (Lawal, 2017). Scoggins *et al.* (2007) also reported a similar domination of heavy PAH concentration. The poorly treated industrial effluent from the nearby area may have contributed to the high mean concentration of PAHs found in the groundwater sample, which may have caused petroleum contamination of the groundwater aquifer. The PAH concentration from the result is consistent with the works of Okoli *et al.* (2011), where the pollution of the water was attributed to the incessant release of refinery effluents into the creeks bordering the coastal settlement.

Table 2: Percentage distribution of PAH homologue in DSC sample site Warri

PAH Homologue	Name	Percentage %
2rings (2R)	Napthalene	3.58
	Acenapthylene	5.86
	Acenapthene	6.11
3rings(3R)	Fluorene	3.87
	Anthracene	4.48
	Phenanthrene	3.22
	Fluoranthene	5.54
4rings (4R)	Pyrene	6.49
	Benz(a)anthracene	2.90
	Chrysene	3.31
5rings (5R)	Benzo(k)fluoranthene	11.17
	Benzo(b)fluoranthene	15.38
	Dibenz(a, h,)anthracene	11.82
	Benzo(a)pyrene	4.19
6rings (6R)	Benzo(g,h,i)pyrene	9.13
	Indeno(1,2,3 – cd)pyrene	2.96

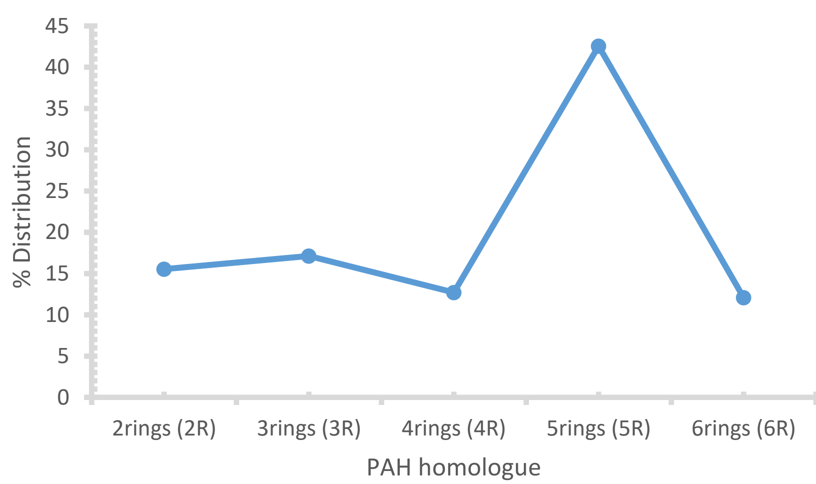

Figure 2: Ring Size Variation of PAHs in DSC Sample Site Warri

4. Conclusion

This study assessed the presence of PAHs in some boreholes at DSC Warri. There were 16 different PAHs found in the sample, which included Naphtalene, Fluorene, pyrene, and Benzo(a)pyrene. The samples contained 16 distinct PAHs, including naphtalene, fluorene, pyrene, and benzo(a)pyrene. This included typical two-ringed and six-ringed PAHs from the various homologues. With the exception of 0.001 mg/L for benzo(a)pyrene, the presence of these PAH chemicals in this investigation was found to be higher than the WHO permitted limit of 0.002 mg/L for drinking water. As a result, this finding raises concerns for public health because it could

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present a number of health risks to those who use these waters. Therefore, in order to prevent negative impacts on both human health and the environment, it will be safe to subject the water to advanced treatment technologies.

Conflict of Interest

The authors hereby declare that there is no conflict of interest whatsoever in this study.

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