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Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) In Underground Water of Girei Basement Complex in Adamawa State, Nigeria

Amina Mohammed Kabiru (Ph.D)[1], Dahiru Hammanjulde Buba[2]

[12]Chemistry Department, Federal College of Education, Yola Adamawa State, Nigeria.

(*)Corresponding Author's: : aminakm57@gmail.com

Abstract

This study assessed the level of polycyclic Aromatic Hydrocarbons (PAHs) in underground water (well and boreholes) use as sources of drinking water in Girei, Adamawa State, Nigeria. Water samples from the study areas were collected from 21 sampling points and analyzed using GC/MS. From the results obtained, acenaphthylene has the highest concentration of 0.091µg/l in well water (WW 10. In borehole water samples, acenaphthylene has the highest concentration of 1.1 in BHW2 and lowest concentration value 0.0081µg/l was recorded in BHW6 and in most of the boreholes. Biphenylene and Fluorene were not detected in both well water and borehole water in the study areas. Generally, the values of PAHs recorded are higher in borehole than in well water. Some of the PAHs values recorded, especially for borehole water were above the tolerable limits of 1µg/l set by FEPA and EU and as a result, effort needs to be intensified toward combating further pollution of drinking water in the study area.

Keywords: Keywords: Organic pollutants, Polycyclic Aromatic Hydrocarbons (PAHs), underground water, basement.

Introduction

In many developing countries, groundwater from boreholes and wells is the most important and reliable resource to meet water needs, highlighting its critical role. These water sources are usually polluted by toxic and hazardous compounds such as polycyclic aromatic hydrocarbons (PAHs) and organic chlorinated pesticides (OCPs) that harm plants and animals [2,3,4, 18] Polycyclic aromatic hydrocarbons (PAHs) represent a widespread class of environmental chemical pollutants and are ubiquitous contaminants with two or more fused aromatic rings in aquatic environments. PAHs are lipophilic compounds with very low water solubility and therefore, their concentrations in water is very low. Lower molecular weight compounds, such as naphthalene, acenaphthene and acenaphthylene, have the highest water solubility while solubility decreases with increasing molecular mass [1]

Health hazards associated with intake of these toxic compounds include neurologic, reproductive and immune defects. Cancer is a primary human health risk of exposure to PAHs. Exposure to PAHs equally causes cardiovascular disease and poor fetal development. PAHs has also been linked to

skin, lung, bladder, liver, and stomach cancers in well-established animal model studies. Some chronic effects of PAHs include Carcinogenicity, Genotoxicity, and Teratogenicity [7]

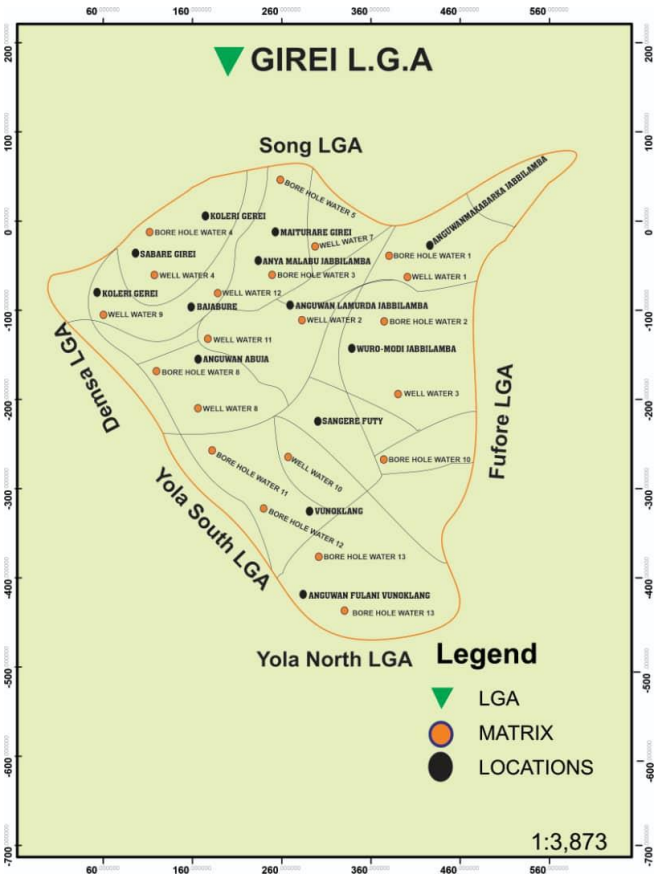
Girei Local Government Area, Adamawa State, Nigeria, is located around the bank of River Benue, where various activities such as farming, fishing, production of foams, dumping of refuse, cabbages to mention just a few is the order of the day. More than 3,000 people have been displaced across Jabbilamba community and environs in Girei LGA, following severe flash flooding from heavy downpours between 18th and 19th August 2024.

According to Sanitation and environmental management agency (SEMA) at least 10 residents were killed and three others wounded in the flash flooding that also damaged or destroyed dozens of homes, critical facilities and livelihoods across the affected areas. Sources have reported the arrival of some of the displaced households in neighboring Song and Yola LGAs as of 22 August 2024 while many homes remain submerged across the affected areas and most residents unable to return to salvage property and valuables (united nations for the coordination of humanitarian affairs 2022). These reasons and many more factors increase the pollution load of the environment. Reassessment of groundwater after a considerable period of time allows us to understand the long-term effects of PAHs contamination, potential changes in contamination levels, and the extent of spread. Additionally, new sources of contamination may emerge within a short period warranting timely intervention to safeguard public health. By assessing health risks and identifying the sources of PAHs, regulatory actions can be taken thereby ensuring community access to safe drinking water [7,12]. Therefore, the aim of this study is to identify eight PAHs present in Girei underground water (well and boreholes) use as sources of drinking water and ascertain their levels of concentrations

Materials and Methods

Description of study areas

The study Area for this research is Girei Local Government of Adamawa State, located in the North Eastern part of Nigeria and lies between latitude 7^{O} and 11^{O}, North of the equator and between longitude 11^{O} and 14^{O}East of the Greenwich meridian [5]. In Girei Local Government Area, well, bore-hole and river water are the major sources of drinking water but two sources (well and borehole water) were the focus in this study.



Fiqure 1:Map of Gerei L.G.A showing sampling points. Source: Urban and Regional Department (MAUTECH)

S/No	Matrix	Locations
1.	Bore hole water 1	Anguwanmakabarka Jabbilamba
2.	Well water 1	Anguwanmakabarka Jabbilamba
3.	Bore hole water 2	Anguwan Lamurda Jabbilamba
4.	Well water 2	Anguwan Lamurda Jabbilamba
5.	Bore hole water 3	Anya Malabu Jabbilamba
6.	Well water 3	Wuro-Modi Jabbilamba
7	Well water 4	Sabare Girei
8.	Bore hole water 4	Sabare Girei
9.	Bore hole water 5	Maiturare Girei
10.	Well water 7	Maiturare Girei
11.	Bore hole water 8	Anguwan Abuja
12	Well water 8	Anguwan Abuja
13.	Well water 9	Koleri Gerei

14.	Bore hole water 10	Sangere Futy
15	Well water 10	Vunoklang
16	Bore hole water 11	Vunoklang
17.	Bore hole water 12	Vunoklang
18.	Bore hole water 13	Vunoklang
19	Well water 11	Bajabure
20	Well water 12	Bajabure
21	Bore hole water 13	Anguwan Fulani Vunoklang

Sample and Sampling Techniques

Water samples were collected from 21 sampling point. The samples collected were mixed thoroughly to form composite samples for replicate analysis. Composite water samples were pre-filtered through 0.45 µm fiber glass filters (Whatman) to remove suspended material and then preserved by the addition of concentrated H_2SO_4 acid to prevent biological activity after which, samples were kept in the refrigeration at a regulated temperature [1,5,7,14]

Samples extraction

The extraction procedures were made in triplicates for each water sample type for the analysis of PAHs using liquid –liquid extraction procedure [14] The liquid –liquid extraction was carried out using separatory funnel. 50 ml of the sample was measured, poured into the funnel and 20ml dichloromethane as equally measured and added to the separatory funnel containing the sample. The mixture was shaken for 30 minutes each and allowed to stand for 5 minutes to separate into phases of organic and aqueous. The organic phases in each case containing the extract were released into a beaker. The extract was further concentrated using steam bath, clean-up passing through anhydrous sodium sulphate and chromatographic grade silica gels (1:3). 2 ml concentrated extract was injected into GC vial sample bottle for GC-MS analysis.

GC-MS Analysis of PAH

The gas chromatographic analysis was performed on a GC (Agilent Technology Model:7890A) interfaced with mass selective detector (Model 5975 MSD). The electron ionization was at a 70v with an ion source temperature at 250^0C. Highly pure helium gas (99.9% purity) was used as carrier gas (mobile phase) while HP-5 (30 mm x 0.25 x 0.320 µm) was used as the stationary phase.

The following were the oven conditions: The oven temperature: 80 ^{o}C (2 min) at the rate of 10 ^{o}C.

Final temperature was 280 ^{o}C (6min) at the rate 11 ^{o}C /minutes, Injection temperature: 250 ^{o}C.

Mobile phase helium gas (99.9% purity) 0.5/mL/min, Column: HP-5 (30 mm X 0.25 mm X 0.320µm), Injection volume: 1µ/L and Mode: Splitless. PAHs constituent were identified by comparing the mass spectra with a known standard.

Quality Control

Blank (pure 99.9% hexane) analysis was done at interval of three control samples for each matrix to ascertain pure baseline and any carry-over sample or analyte to the next sample. Another control measure adopted to validate the conditionality of the entire systems was the analysis of known reference standards as sample to address the efficiency of the instrument.

Statistical analysis

All analysis was carried out in triplicates. Method validation for this study were maintained at LSD ±5% and percentage recoveries were calculated. Data obtained were subjected to analysis of variance (ANOVA) using SPSS version 22 to determine the differences in the concentration of each of the organochlorine pesticides residue in each sample analyzed (US EPA, 2010).

Results and Discussion

Table 1: Mean Concentrations Levels (µg/L) of Organic Pollutants (PAHs) in Drinking Water (Wells) in the Study

Compounds	WW1	WW2	WW3	WW4	WW5	WW6	WW7	WW8	WW9	WW10
Acenaphthylene	0.07± 0.014	0.12± 0.014	0.01 ± 0	0.13± 0.014	0.07± 0.01	0.1± 0.02	0.02± 0.01	0.01± 0.01	0.07±0 .02	0.09± 0
Naphthalene	0.01± 0.032	0.01± 0.06	0.01± 0.01	0.01± 0.06	0.01± 0.031	0.01± 0.05	ND 0	0.01± 0.01	0.01± 0.031	0.01± 0.042
Fluoranthene	0.02± 0.016	0.01± 0	ND 0	0.02± 0.016	ND 0	0.02± 0.013	0.01± 0	ND 0	0.01± 0.008	ND 0
Biphenylene	ND 0	ND 0	ND 0	ND 0	ND 0	ND 0	ND 0	ND 0	ND 0	ND 0
Acenaphthene	0.01± 0.01	0.01± 0	0.01± 0	0.01± 0.01	0.01± 0	0.01± 0	0.01± 0	0.01± 0	0.01± 0.01	0.01± 0
Fluorene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Phenanthrene	0.01± 0	0.05± 0.016	0.04± 0.008	0.04± 0	0.01± 0	0.03± 0.014	0.01± 0	0.01± 0	0.01± 0	0.01± 0
Anthracene	0.01± 0	0.01± 0.01	0.01± 0	0.04± 0.01	0.01± 0	0.01± 0	0.01± 0	0.01± 0	ND 0	ND 0
Benzo[k]fluoranthene	0.37±	0.23±	0.12±	0.48±	0.52±	0.85±	0.50±	0.45±	0,17±	0.13±

Table 2: Mean Concentrations Levels (µg/L) of Organic Pollutants (PAHs) in Drinking Water (boreholes) in the Study

Compounds	BHW 1	BHW 2	BHW3	BHW 4	BHW 5	BHW6	BHW 7	BHW8	BHW9	BHW10	BHW11
Acenaphthylene	0.13± 0.02	1.1± 0.01	0.07± 0.01	0.21± 0.02	0.09± 0.014	0.04± 0	0.05± 0.004	0.07± 0.004	0.07± 0.014	0.1± 0	0.07± 0.014
Naphthalene	0.02± 0.057	0.01± 0.545	ND 0.035	0.02± 0.097	0.01± 0.041	ND 0.019	ND 0.024	0.01± 0.033	ND 0.032	0.01± 0.047	0.01± 0.031
Fluoranthene	0.01± 0	0.01± 0.008	ND 0	0.04± 0.016	0.01± 0	0.01± 0	ND 0	ND 0	0.02± 0	0.02± 0.008	0 0
Biphenylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acenaphthene	0.01± 0	0.01± 0.008	0 0.014	0.01± 0	0 0.014	0.01± 0.008	0 0.014	0.01± 0.008	0.01± 0	0 0.014	0.01± 0
Fluorene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Phenanthrene	0.08± 0.008	0.01± 0	0 0.014	0.04± 0	0.02± 0.008	0.01± 0	0.01± 0.008	0.01± 0	0.01± 0	0.01± 0	0.01± 0
Anthracene	0.08± 0.01	0.01± 0	0.01± 0	0.01± 0	0.01± 0	ND 0	0.01± 0	ND 0.014	0.02± 0.01	ND 0	0.01± 0
Benzo[k]fluoranthene	0.75±	0.47±	0.07±	1.19±	0.79±	1.18±	0.06±	0.04±	0.5±	0.54±	0.58±

Table 1 present the results obtained for the PAHs analyzed in the different wells sampled. The results show that acenaphthene has the highest concentration of 0.09µg/L in WW10. Naphthalene was 0.01 µg/L in the wells sampled except for WW7. Flouranthenee highest concentration is 0.01 µg/L in WW7, Biphtnalene is not detected, Acenaphthene have same concentration values of 0.01 µg/L all through the samples while Fluorene was equally not detected. Phenanthrene highest concentration is 0.05 µg/L in WW2 and lowest

value of 0.04 µg/L in most wells/ Anthracene highest value of 0.01 µg/Lis in WW4 but not detected in WW 9 and WW 10. Benzo(k)Fluoranthene highest value is 0.85 µg/L is obtained in WW6 while its lowest concentration of 0.12 µg/L is in WW3.

Though, most of PAHs recorded in this study were within the tolerable limits of 1ug/l for human consumption and 0.5 ug/l for children toys set by FEPA, EU and United States, Environmental Protection Agency (US EPA). respectively. The presence of organic pollutant in the drinking water across the area is an indication of unsafe drinking water for both human and animal consumption. It is also an indication that human activities contribute to their availability in both wells and boreholes. This agreed with conclusion drawn by [14] that though PAH2s are organic chemical compounds that can occur naturally in the environment but their occurrence can be accelerated by anthropogenic activities. [12] established that there are high and persistent environmental contaminants through PAHs which was due to their existence in various combinations and ubiquity.

The current study recorded most of PAH at low concentration in the drinking water, this could be as a result of its hydrophobicity which make solubility of PAHs to decreases while in water with increase in molecular weight. This agreed with the submission made by [20] that the only reason for low concentration of PAHs in water is due to reduction in solubility. Thus, the low concentration as recorded in most of the studied drinking water sources is an indication of pollution. Also, study by [11] maintained that though, PAHs are mostly found at low concentration in water and environment due to their low biodegradability but it highly difficult to be eliminated after discovery.

The sources of PAHs in the study Area are likely to be more of anthropogenic activities than natural. Activities such as combustion of crude oil and petroleum spills, industrial and municipal waste and wastewater which represent the anthropogenic environmental inputs are likely the sources of PAHs in the study Area. This agrees with the conclusion drawn by [12] that in most developing nation, unsafe practices in the farmland, industries and water usage pattern remains the main sources of PAHs.

Table 2 presents the results obtained for the PAHs analyzed in the different boreholes sampled. On table, acenaphthylene has the highest concentration of 1.1 µg/L in BHW2 and lowest concentration value is in BHW6, Naphthalene highest value was in BHW1, not detected in BHW 3,6,7 and 9 and lowest value in BHW11. Fluoranthene highest concentration is in BHW 4, not detected in BHW 3, 7, 8, lowest value in BHW 1. Biphenylene was not detected in any of the bore hole water sample. Acenaphthane had same concentration of 0.01µg/L all through while Fluorene was equally not detected. Phenanthrene highest concentration was 0.05µg/L in BHW1 and lowest value of 0.04µg/L BHW3. Anthracene highest value of 0,01µg/L was

in BHW1 not detected in BHW 6, 8, and 10. but with lowest value of 0.04µg/L in BHW 11. Benzo{k}Fluoranthene highest value of 0.85µg/L was obtained in BHW4 and lowest value was 0.12µg/L in BHW2.

Most of the PAHs recorded in this study were within the tolerable limits of 1ug/l for human consumption and 0.5 ug/l for children toys set by FEPA and EU respectively in well water but concentration in borehole water were higher than the tolerant values.

In a similar work carried out by [12]**,** in Nsisioken-Agbi Ogale, a Niger Delta community PAHs were detected in all samples except BH3 at concentrations ranging from ND to 2.0 µg/L. Only five of the sixteen PAH pollutants were detected in the test samples, with a mean total concentration of 5.8 ± 2.3 µg/L. Fluoranthene has the highest mean concentration of 8.5 ± 2.13 µg/L, followed by chrysene (7.5 ± 2.12 µg/L), pyrene (7.0 ± 2.84 µg/L) and benz[a]anthracene (5.5 ± 3.54 µg/L), while benzo(b)fluoranthene has the lowest mean concentration (0.5 ± 0.71 µg/L). The mean PAH concentration ranged from N.D. in BH3 to 9.0 µg/L in W3. W1, W2, W3 showed a higher PAH concentration with a ΣPAH concentration of 8.0 µg/L compared to the borehole water, which had a total ΣPAH concentration of 2.5 µg/L. No PAH was detected in BH3..

A comprehensive study of PAHs in three household dug wells and three boreholes was conducted using Agilent 7890B gas chromatography and 5975A mass spectrometry. The detected PAHs were mainly 4 - 5 ringed PAHs, such as Chrysene, Fluoranthene, Pyrene, Benzo[a]anthracene, and Benzo[b]fluoranthene. The total mean concentration was 5.8 ± 2.3 µg/L, with values ranging from not detected in borehole 3 to 8.0 µg/L at well 2. Source identification analysis suggested that the PAHs originated from fuel and biomass combustion which is agreement with the present study conducted in Girei local Government Area. The availability of PAHs in their drinking water is associated with geological factors such as rocks, erosion, farming activates etc. Flooding which is a yearly phenomenon in the study area is another source of PAHs in water sources. This is evident from the various concentration values obtained especially for the BHW.

Conclusion

In conclusion, the results indicated that acenaphthylene has the highest concentration of 0.091 µg/l in the well water (WW 10). In borehole water samples, acenaphthylene has the highest concentration of 1.1 in BHW2 and the lowest concentration value 0.0081µg/l was recorded in BHW6 and in most of the boreholes. Further, Biphenylene and Fluorene were not detected in both well water and borehole water in the study areas. Generally, the values of PAHs recorded are higher in borehole than in well water.

Therefore, the presence organic pollutant in the drinking water across the sampled points studied is an indication of unsafe drinking water for both human and animal consumption. It is also an

indication that human activities contribute to their availability in both wells and boreholes water which are their major drinking water sources.

Nigeria is yet to come up with safe margins as standards for PAHs level in food items and water, rather the nation is depending on the mindless lifting of foreign safe limit values for the protection of the differential Local ecosystems.

However, recently the regulatory bodies such as National Agency for Food and Drug Administration and Control (NAFDAC) and Standard Organization of Nigeria (SON) have stood up for regulation of different food and water substance as well as permissible limits. It has become necessary to promptly focus on PAHs and POPs in both food and water.

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