FUDMA Journal of Sciences (FJS)
ISSN online: 2616-1370
ISSN print: 2645 - 2944
Vol. 9 No. 2, February, 2025, pp 152 - 157
DOI: https://doi.org/10.33003/fjs-2025-0902-3140

DETERMINATION OF PAHS IN UNDERGROUND WATER USING GC-MS AND GC-FID IN OSUN STATE, SOUTHWEST NIGERIA

***[1]Ediagbonya, T. F, [2]Uche, J. I. and [1]Olojo, D. D.**

[1]Department of Chemical Sciences, Olusegun Agagu University of Science and Technology, Okitipupa, Ondo State, Nigeria.
[2]Department of Chemical Sciences, University of Delta, Agbor Delta State, Nigeria

*Corresponding authors' email: tf.ediagbonya@oaustech.edu.ng Phone: +2348086809323

ABSTRACT

Contamination of underground water by polycyclic aromatic hydrocarbons (PAHs) poses significant health risks, yet the effectiveness of different analytical methods in detecting these contaminants remains unclear. This study compares the sensitivity of Gas Chromatography-Mass Spectrometry (GC-MS) and Gas Chromatography-Flame Ionization Detection (GC-FID) in analyzing PAH concentrations in borehole and well water in Osun State, Nigeria. Results showed that GC-MS detected a broader range of PAHs (22 compounds) compared to GC-FID (13 compounds), highlighting its higher sensitivity. While GC-FID recorded higher PAH concentrations in borehole samples, GC-MS provided a more precise differentiation of compounds. These findings emphasize the importance of selecting an appropriate detection method to accurately assess PAH contamination in drinking water, which is crucial for environmental monitoring and public health safety.

Keywords: GC-MS, GC-FID, Polycyclic aromatic hydrocarbons, Underground water contamination, Water quality assessment

INTRODUCTION

Large levels of organic pollutants have been identified in several water sources as a result of various natural disasters and man-made activities. Organic pollutants in water are frequently carcinogenic and toxic, raising concern around the world. (Gorji *et al,* 2016; Khalili *et al,* 2021; Kiani *et al,* 2021;Ediagbonya *et al*,2024ab). Organic pollutants, particularly PAHs, are found in the oil, gasoline, coal, wood, natural forest fires, transit trucks, trash incineration, volcanic eruptions, and processes (foundries, steel, aluminum and iron production) in the environment, especially running water (Roudbari *et al,* 2021; Shariatifar *et al,* 2021). Polycyclic aromatic hydrocarbons (PAHs) are multi-ringed chemical molecules that are abundant in nature. So far, more than a hundred PAHs have been discovered in nature, 16 of which [(indeno[1,2,3-cd]pyrene (IP), benzo(b)fuoranthene (BbF), benzo(a)pyrene (BaP), chrysene (Ch), benzo(k)fuoranthene (BkF), naphthalene (NA), pyrene (P), phenanthrene (Pa), benzo(a)anthracene (BaA), acenaphthylene (Ace), acenaphthene (Ac), fuoranthene (Fl), fluorene (F), anthracene (A), benzo[g,h,i]perylene (BgP) and dibenzo[a,h]anthracene (DhA)] have been classified by US-EPA (USA Environmental Protection Agency) as pollutants (Chen *et al,* 2016; Duedahl-Olesen *et al,* 2015). Due to their physical and chemical properties, the most widely used analytical separation techniques for PAH determination have been gas chromatography with flame ionization detector (GC-FID), mass spectrometry (GC–MS), high-performance liquid chromatography (HPLC) with UV–visible detector, diode array (DAD), fluorescence detector and supercritical fluid chromatography (SFC), which can also be associated with other types of detectors (Geiss *et al,* 2018; Makós *et al,* 2018). Chromatography represents the most prominent set of analytical techniques for PAH determination at present time. FID offers good sensitivity to a range of VOC classes and has the advantage of being relatively simple to operate, but identification of active compounds is limited to information about their Kováts retention indices and the shape of peaks. More accurate identification of active compounds requires analysis of samples on a GC coupled to a mass spectrometer (GC-MS). This step can be difficult and time-consuming because chromatograms derived from FID are not identical to those derived from MS (due to their compound-specific differences in sensitivity), and because differences in column parameters and detector operating pressures (atmospheric versus vacuum) induce variation in relative retention times which can make it challenging to link peaks from the FID chromatogram to those of the total ion chromatogram (TIC) from the MS. A further limitation is that some sampling methods, such as thermal desorption and solid-phase micro extraction (SPME), require that the entire sample be used for a single injection, so sampling has to be replicated to generate a second injection on GC-MS (Li *et al,* 2021).

MATERIALS AND METHODS

Description of the study area

This research was carried out at Osogbo, the capital city of Osun State, Nigeria. It lies on coordinate 7˚46ʹ north 4˚34ʹ east with an area of 47kmsq. Osogbo city seats the Headquarters of both Osogbo Local Government Area (situated at Oke-Baale Area of the city) and Olorunda Local Government Area (situated at Igbonna Area of the city). The city had a population of about 500,000 people. Osogbo is a commercial and industrial centre that has experienced rapid urbanization and industrialization. This urban development may contribute to the generation and release of various pollutants, including PAHs, into the environment, potentially affecting groundwater quality.

Sampling method

A total of six (6) samples of water were collected from underground water in Oke-Ayepe area of Osogbo, Osun state. Three samples from the well, and three samples from the borehole using clean, non-contaminated containers. Exposure to air and light was minimized. This is because PAHs can degrade when exposed to light. Before sampling, sample bottles and storage glass wares were washed with detergent, rinsed with distilled water and then dried in an oven overnight at 100˚C. Sampling bottles were used in collecting water samples for the determination of PAHs. The water sample was filtered to remove particulate matter. For 22 PAHs extraction from underground water samples, liquid-liquid extraction was used.

Table 1: Co-ordinate of Sampling Sites

Site Code	Sources	Latitude	Longitude	Location
A	Well	7.47507N	4.34087E	Osun state
B	Borehole	7.47507N	4.34087E	Osun state
C	Well	7.758410N	4.568829E	Osun state
D	Borehole	7.758410N	4.568829E	Osun state
E	Well	7.791198N	4.516614E	Osun state
F	Borehole	7.758410N	4.516614E	Osun state

Instrumentation

Agilent 7820A gas chromatograph coupled to 5975C inert mass spectrometer (with triple axis detector) with electron-impact source (Agilent Technologies) was used. The stationary phase of separation of the compounds was HP-5 capillary column coated with 5% Phenyl Methyl Siloxane (30 m length x 0.32 mm diameter x 0.25 µm film thickness) (Agilent Technologies). The carrier gas was Helium used at a constant flow of 1.2 mL/min at an initial nominal pressure of 026 psi and average velocity of 40.00 cm/sec. 1µL of the samples were injected in splitless mode at an injection temperature of 250 °C. Purge flow to spilt vent was 30.0 mL/min at 0.35 min with a total flow of 31.24 mL/min; gas saver mode was switched off. The oven was initially programmed at 110 °C (1 min) and then ramped at 15°C/min to 310 °C (3 min). The run time was 16 min with a 3 min solvent delay. The mass spectrometer was operated in electron-impact ionization me at 70 eV with ion source temperature of 230 °C, quadrupole temperature of 150 °C and transfer line temperature of 300 °C. Acquisition of ion was via Scan mode (scanning from m/z 35 to 550 amu at 2.0s/scan rate) and selective ion mode (SIM).

A GC-2010 Plus AF (Shimadzu, Kyoto, Japan) was used for chromatographic separations and determinations. The GC system contained a split/splitless injector (SPL-2010 Plus) and an FID detector (FID-2010 Plus). It was run with a GC solution software. The GC separations were performed using a BPX-5 fused silica capillary column (30 m x 0.25 mm i.d., 0.25 mm film thickness). To achieve the best separation conditions and retention times for BTEX and PAHs, different temperature programs were examined. The optimized column temperature program started at 40˚C and then ramped to 70˚C at a rate of 6˚C min^{-1}. Afterwards, the temperature was increased to 160˚C (at a rate of 50˚C min^{-1}) and then raised to 240˚C (at a rate of 10˚C min^{-1}) and held constant for 2 min. Finally, the temperature was increased to 280˚C (at a rate of 30˚C min^{-1}) and remained constant for 3 min. Accordingly, the total GC run time was 21.3 min. The injector and detector were maintained at 280 and 320˚C, respectively.

RESULTS AND DISCUSSION

Table 2: Mean comparison of PAHs using GC-MS and GC-FID at borehole sample

PAHs	GC-MS	GC-FID	T	P
NAPHTHALENE	0.64±0.03	0.69±0.02	-3.165	0.013
ACENAPHTHYLENE	0.83±0.02	1.36±0.04	-27.526	0.000
ACENAPHTHENE	0.52±0.01	0.94±0.02	-50.440	0.000
FLUORENE	0.23±0.01	0.99±0.02	-77.176	0.000
PHENANTHRENE	1.10±0.04	0.56±0.01	29.889	0.000
ANTHRACENE	1.21±0.03	0.71±0.01	38.576	0.000
FLUORANTHENE	1.08±0.03	0.44±0.01	50.916	0.000
PYRENE	1.21±0.03	0.62±0.01	45.597	0.000
BENZO(C)PHENANTHRENE	0.70±0.02	0.80±0.01	-9.697	0.000
BENZ(a)ANTHRACENE	1.49±0.02	0.81±0.02	62.623	0.000
CHRYSENE	0.77±0.01	7.97±0.03	-522.488	0.000
BENZO(e)PYRENE	1.61±0.02	BDL		
BENZO(k)FLUORANTHENE	1.13±0.01	BDL		
BENZO(b)FLUORANTHENE	1.91±0.02	BDL		
3-METYHYLCHLORANTHRENE	2.67±0.02	1.92±0.02	57.676	0.000
INDENO[1,2,3-cd]PYRENE	1.75±0.02	BDL		
DIBENZY(9,h)ANTHRANCENE	0.15±0.01	BDL		
BENZO(ghi)PERYLENE	2.15±0.02	BDL		
DIBENZO(a,h)PYRENE	1.70±0.02	BDL		
DIBENZO(a,i)PYRENE	1.70±0.02	BDL		
DIBENZO(a,l)PYRENE	1.82±0.02	BDL		
BENZO(a)PYRENE	0.27±0.01	1.56±0.02	-117.213	0.000

The results of the comparison of the mean values of PAHs in borehole water are shown in Table 2. Comparison of the mean PAH values revealed a consistent and statistically significant trend: GC-FID consistently yielded higher mean concentrations of PAH compounds in comparison to GC-MS. Specifically, mean differences were observed across a spectrum of PAHs, including Acenaphthylene (0.53), Acenaphthene (0.42), Fluorene (0.76), Phenanthrene (0.54), Anthracene (0.50), Fluoranthene (0.64), Pyrene (0.59), Benzo(c)phenanthrene (-0.10), Benzo(a)anthracene (0.68), and Chrysene (-7.20). These differences, represented in parentheses, are statistically significant (all p-values < 0.001), underscoring the substantial methodological impact on the recorded levels of PAHs. A higher GC-FID value suggested the presence of other carbon-containing compounds (impurities or co-eluting Compounds) in the sample that the GC-MS can distinguish but the GC-FID cannot. (Roudbari *et al*, 2021,). GC-MS was able to detect all 2 PAHs while GC-FID was able to detect only 13 PAHs, having 9 PAHs below the detection limit. This makes GC-MS more sensitive than GC-FID (Fabio *et al* 2019). in addition, Lezzaik *et al*, (2021) also reported a higher range for GC-FID compared to the GC-MS.

It is noteworthy that certain PAH compounds exhibited remarkable agreement between the two analytical methods. For instance, Benzo(b)fluoranthene exhibited virtually identical mean values (0.00) for both GC-MS and GC-FID, indicating high methodological consistency. Similarly, Benzo(a)pyrene displayed minimal differentiation, with a mean difference of 0.01, and the "t" test indicated non-significant differences (p > 0.05). These findings are supported by a "t" test indicating non-significance (p > 0.05), signifying the absence of noteworthy interference or co-elution of other compounds, as reported by Shariatifar *et al*. in 2022. In the comparison of the total PAH levels in borehole water samples at Osogbo with reports of borehole samples located in other sites in other regions, high levels of PAHs higher than the study areas were found in Abia and Imo, Nigeria (Onydinma *et al*, 2021), Rivers, Nigeria (Ogbuagu *et al*, 2011).

Table 3: Mean comparison of PAHs using GC-MS and GC-FID at well water sample

PAHs	GC-MS	GC-FID	T	P
NAPHTHALENE	1.97±0.07	1.41±0.02	18.035	0.000
ACENAPHTHYLENE	0.31±0.02	1.06±0.01	-67.902	0.000
ACENAPHTHENE	2.95±0.06	1.12±0.01	70.412	0.000
FLUORENE	3.82±0.05	1.13±0.01	120.300	0.000
PHENANTHRENE	1.68±0.02	0.55±0.01	123.511	0.000
ANTHRACENE	1.12±0.02	0.47±0.01	75.328	0.000
FLUORANTHENE	0.52±0.02	0.52±0.01	0.000	1.000
PYRENE	6.48±0.02	0.58±0.02	455.195	0.000
BENZO(C)PHENANTHRENE	4.09±0.03	0.77±0.01	280.760	0.000
BENZ(a)ANTHRACENE	4.90±0.04	0.75±0.01	243.344	0.000
CHRYSENE	5.43±0.04	5.01±0.01	24.364	0.000
BENZO(e)PYRENE	0.81±0.02	BDL		
BENZO(k)FLUORANTHENE	2.71±0.03	BDL		
BENZO(b)FLUORANTHENE	2.64±0.03	BDL		
3-METYHYLCHLORANTHRENE	1.59±0.02	2.14±0.03	-31.649	0.000
INDENO[1,2,3-cd] PYRENE	1.88±0.03	BDL		
DIBENZY(9,h)ANTHRANCENE	6.29±0.06	BDL		
BENZO(ghi)PERYLENE	1.82±0.03	BDL		
DIBENZO(a,h)PYRENE	2.08±0.03	BDL		
DIBENZO(a,i)PYRENE	2.69±0.04	BDL		
DIBENZO(a,l)PYRENE	1.35±0.02	BDL		
BENZO(a)PYRENE	0.34±0.01	0.83±0.02	-55.482	0.000

The mean values of the GC-MS and GC-FID analysis for well water (table 3) unveiled significant differences across various PAH compounds. For instance, Naphthalene exhibited a mean concentration of 1.97 ± 0.07 when measured with GC-MS, while GC-FID reported a lower concentration of 1.41 ± 0.02. This discrepancy was statistically significant, favoring GC-MS. Conversely, Acenaphthylene displayed a marked difference, with GC-FID recording a substantially lower mean concentration of 0.31 ± 0.02 compared to GC-MS at 1.06 ± 0.01. The difference strongly favored GC-MS. Similar patterns emerged for Acenaphthene, Fluorene, Phenanthrene, and Anthracene, with GC-MS consistently reporting higher concentrations compared to GC-FID. These differences were statistically significant (all p values < 0.001), emphasizing the methodological impact on PAH level determination. However, some compounds, such as Fluoranthene, exhibited remarkable methodological consistency, with both GC-MS and GC-FID yielding virtually identical mean values. In these cases, the difference was non-significant (p = 1.000). A lower GC-FID value suggests that some PAHs are present at lower concentrations in the sample and are not easily detected by GC-FID, while GC-MS provides more sensitive detection for those compounds (Makós *et al*,2018). Remarkably, Fluoranthene registers nearly identical mean values with both methods, resulting in a statistically non-significant difference (t = 0.000, p = 1.000). The difference in Gas Chromatography with Flame Ionization Detector (GC-FID) and Gas Chromatography-Mass Spectrometry (GC-MS) results for the two underground water sites (BH and WW) can be indicative of the types and concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) present in the samples. (Teimoori *et al*. 2023; Thamatam *et al*, 2023). Certain PAHs occur at low environmental concentrations due to their low biodegradability and elimination problems. (Adeniji *et al*, 2019).

Table 4: Comparison of results of this study (mean concentrations of PAHs) using GC-MS with similar studies in other parts of the world

Location	Number of PAHs	Range(mg/l)	References
This Study	22	6.48	This study
Osun Nigeria	7	BDL- 0.12	Abolanle *et al*, 2017
Lagos, Nigeria	13	0.1- 73.72	Ogunfowokan *et al* 2003
Osogbo, Nigeria	16	0.1 – 15.81	Ogunfowokan *et al* 2003
Jos, Nigeria	16	0.006 – 9.5	Uzochukwu 2017
Taiwain, China	16	0.07 – 0.14	Chih-Feng *et al*, 2019
Sergipe, Brazil	16	0.096 – 1.39	Dorea *et al*, 2006

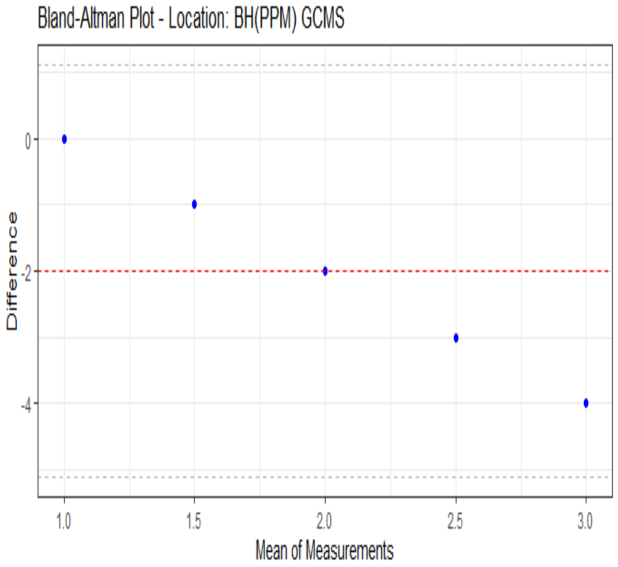
The highest total PAHs concentration in water sample determined by GC-MS in this study is 6.48 and it was significantly higher than those reported in researches carried out in Osun, Nigeria (Abolanle *et al*, 2017), Taiwan, China (Chih-Feng *et al*, 2019), Sergipe, Brazil (Dprea *et al*, 2006); but lower than those reported in Lagos, Nigeria; Osogbo, Nigeria (Ogunfowokan *et al*, 2003); Jos, Nigeria (Uzochukwu, 2017). The proximity of these sites to the point source is responsible for the high level of water contamination in these regions. The highest level of PAHs which was 73.72 was found in Lagos because of the high traffic density on the road and high industrial activity in the vicinity of the latter site (Ogunfowokan *et al*, 2003). GC-MS was seen to be able to detect all PAHs from other studies except for Osun Nigeria. It can be deduced that the PAHs detected in groundwater samples in wet and the dry seasons in Osun, Nigeria were light PAHs. Heavy PAHs are rarely present in water; this is due to the low water solubility of these compounds (Anyakora *et al*, 2003).

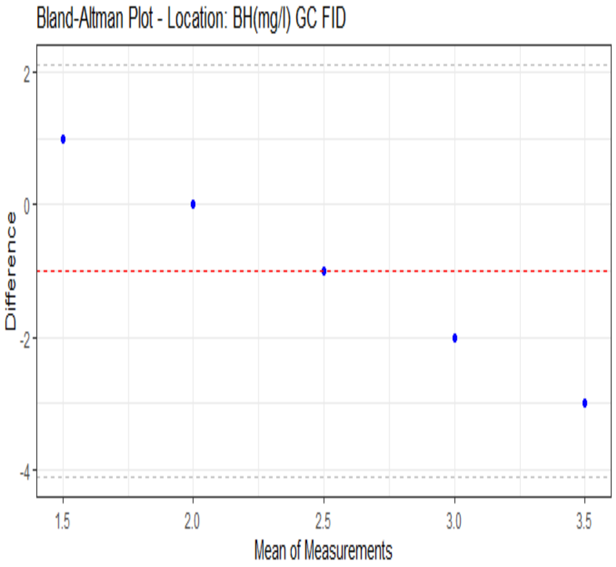
Table 5: Comparison of results of this study (mean concentrations of PAHs) using GC-FID with similar studies in other parts of the world

Location	Number of PAHs	Range	References
Osun, Nigeria	22	BDL-7.97	This study
Abia & Imo, Nigeria	16	BDL-0.03	Ukaogo et al 2021
Ondo, Nigeria	10	0.11-0.34	Olajire et al 2007
Para, Brazil	16	0.005-0.5	Fabio et al 2019

The highest total PAHs concentration in water determined by GC-FID in this study is 7.97 and it was significantly higher than those reported in research carried out in Abia & Imo state, Nigeria (Ukaogo *et al*, 2021); Ondo, Nigeria (Olajire *et al*, 2007); Para, Brazil (Fabio *et al*, 2019).

The fig1 below shows the Bland-Altman plot. The Bland-Altman approach was rapidly adopted in analytical chemistry. Comparison of results obtained by two analytical methods yields different quantitative results (Dimitrios 2023) Bland-Altman plot is a useful tool used to check agreement between two measurements when two instruments are measuring a particular outcome identifying discrepancies between measurements. This graph shows that the GC-MS and GC-FID are quite close in their measurement.





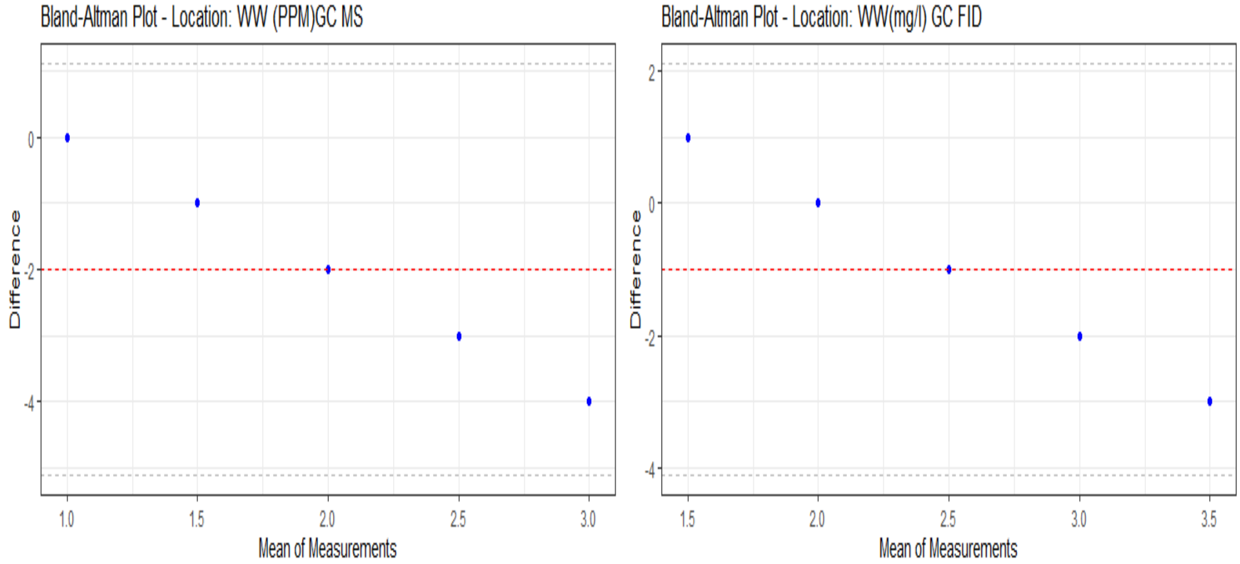


Figure 1: Bland-Alman Plot of GC-MS and GC-FID

CONCLUSION

The Study explored the quantification of Polycyclic Aromatic Hydrocarbons (PAHs) in underground water, utilizing Gas Chromatography-Mass Spectrometry (GC-MS) and Gas Chromatography with Flame Ionization Detection (GC-FID) techniques. The findings reveal significant disparities between the two analytical methods, highlighting the importance of selecting the appropriate technique for accurate PAH quantification. In the case of BH, GC-FID consistently reported higher PAH concentrations than GC-MS for most compounds, signifying potential interference or co-elution of other carbon-containing compounds that GC-MS can differentiate. Contrastingly, the analysis of WW samples revealed a different outcome, with GC-FID consistently yielding lower PAH concentrations compared to GC-MS. This discrepancy may suggest that GC-MS is more sensitive in detecting certain PAH compounds present at lower concentrations. The variations in PAH concentrations between BH and WW samples may reflect the unique composition and sources of PAHs in these underground water sources. This study underscores the importance of carefully selecting the analytical method when quantifying PAHs in underground water.

RECOMMENDATION

It is recommended that when selecting an instrument for quantifying Polycyclic Aromatic Hydrocarbons (PAHs) in underground water, the sensitivity of the instrument should be considered. GC-MS offers higher sensitivity when compared to GC-FID. It can detect a wide range of PAH compounds with different masses and structures.

REFERENCES

Abolanle S.A., John A.O.O., Oluwaseyi S.O., Nobanathi W. M. B., Godwin O.O., Olaoluwa R.O. (2017). Determination of polycyclic aromatic hydrocarbon levels of groundwater in Ife north local government area of Osun state, Nigeria, / Toxicology Reports, 4 39–48.

Adeniji, A. O., Okoh, O. O., &Okoh, A. I. (2019). Distribution pattern and health risk assessment of polycyclic aromatic hydrocarbons in the water and sediment of Algoa Bay, South Africa. *Environmental geochemistry and health*, 41, 1303-1320.

Anyakora C.A., Ogbeche K.A., Palmer P., Coker H., Ukpo G., Ogah C. (2004). A screen for Benzo(a)pyrene, a carcinogen: in the water samples from the Niger Delta region, *Nig. J. Hosp. Med.* 14 (2004) 288–293.

Chen H, Gao G, Liu P, Pan R, Liu X, Lu C (2016) Determination of 16 polycyclic aromatic hydrocarbons in tea by simultaneous dispersive solid-phase extraction and liquid–liquid extraction coupled with gas chromatography–tandem mass spectrometry. *Food Anal Methods* 9:2374–2384.

Chih-Feng C., Yun-Ru J., Yee C. L., Shu-L.H., Mei-Ling T., Pei-Pei S., Ravi K., Chiu-Wen C., and Cheng-Di D. (2019), Determination of Polycyclic Aromatic Hydrocarbons in Sludge from Water and Wastewater Treatment Plants by GC-MS, *Int. J. Environ. Res. Public Health*, 16, 2604.

Dorea, H.S., Bispo. J.R.L., Arago, K.A.S., Chuna, B.B., Navickiene,. S., Alves,j.p.h., Garcia, C.A.B. (2007). Analysis of BTEX, PAHs and metal in the oilfield produced water in the brazil. *Microchemical journal*, 85(2), 234-238.

Dimitrios T (2023), GC-MS measurement of malondialdehyde (MDA) in clinical studies: Pre-analytical and clinical considerations, *Journal of mass Spectrometry and Advances in the clinical Lab 30*:10 – 24. https://doi.org/10.1016/

Duedahl-Olesen L, Navaratnam MA, Jewula J, Jensen A (2015) PAH in some brands of tea and cofee. *Polycycl Aromat Compd* 35:74–90

Ediagbonya, T. F., Omokungbe, O.R., Bagbe ,A. S., Ajibare, O. A., Akinola, T.M., Obebe., F. C. (2024a) An assessment of the risks related to polychlorinated biphenyls (PCBs) in sediments, water, and Prawn (*Nematopaleamon Hastatus*) in Araromi Beach, Ondo State, Nigeria. Toxic and Environ Health 29;1-16

Ediagbonya, T. F., Francis, S. D., Omotayo-Tomo, M.S.,Oziegbe, F. E., Awojobi, O A (2024b) Risk Assessment and Quantification of Elemental Concentrations in River and Stream in Nigeria . Discover Toxicology.2:;1-16

Fabio I. M., Heronides A.D., Kellydas G.F. (2019). Simultanueous determination of 16 polycyclic aromatic hydrocarbons in groundwater by GC-FID after solid-phase extraction, SN *appl. sci* 1, 804.

Geiss O, Senaldi C, Bianchi I, Lucena A, Tirendi S, Barrero-Moreno J (2018) A fast and selective method for the determination of 8 carcinogenic polycyclic aromatic hydrocarbons in rubber and plastic materials. *J Chromatogr A* 1566:13–22

Gorji M.E.H., Ahmadkhaniha R, Moazzen M, Yunesian M, Azari A, Rastkari N (2016) Polycyclic aromatic hydrocarbons in Iranian Kebabs. Food Control 60:57–63.

Khalili F, Shariatifar N, Dehghani MH, Yaghmaeian K, Nodehi RN, Yaseri M (2021) The analysis and probabilistic health risk assessment of polycyclic aromatic hydrocarbons contamination in vegetables and fruits samples marketed Tehran with chemometric. *Glob Nest J* 23:1–12.

Kiani A, Ahmadloo M, Moazzen M, Shariatifar N, Shahsavari S, Arabameri M, Hasani MM, Azari A, Abdel-Wahhab MA (2021) Monitoring of polycyclic aromatic hydrocarbons and probabilistic health risk assessment in yogurt and butter in Iran. *Food Sci Nutr* 9:2114–2128.

Li, J., Wu, J., Wang, Y., Wu, Y., & Yang, L. (2022). Determination of polycyclic aromatic hydrocarbons in underground water using GC-FID and GC-MS with improved sensitivity and selectivity. *Environmental Science and Pollution Research International*, 29(12), 14461-14472.

Makós P, Przyjazny A, Boczkaj G (2018) Hydrophobic deep eutectic solvents as "green" extraction media for polycyclic aromatic hydrocarbons in aqueous samples. *J Chromatogr A* 1570:28–37

Ogbuagu, D. H., Okoli, C. G., Gilbert, C. L., &Madu, S. (2011). Determination of the contamination of groundwater sources in Okrika Mainland with Polynuclear Aromatic Hydrocarbons (PAHs). *British Journal of Environment and Climate Change,* 1(3), 90-102

Olajire A., Alade A.O, Adeniyi A.A., Abemiwo O.M. (2007). Distribution of polycyclic aromatic hydrocarbons in surface soils and water from the vicinity of Agbabu bitumen field of southwestern Nigeria, *J. Environ. Sci. Health* 42 (8) 1043–1049.

Ogunfowokan, A.O., Asubiojo, O.I. & Fatoki, O.S. (2003). Isolation and determination of polycyclic aromatic hydrocarbon in surface runoff and sediments. *Water, air & soil pollution.* 147, 245-261

Onydinma, U. P., Aljerf, L., Obike, A., Onah, O. E., & Caleb, N. J. (2021). Evaluation of physicochemical characteristics and health risk of polycyclic aromatic hydrocarbons in borehole waters around automobile workshops in Southeastern Nigeria. Groundwater for Sustainable Development, 14, 100615.

Roudbari A, Nazari RR, Shariatifar N, Moazzen M, Abdolshahi A, Mirzamohammadi S, Madani-Tonekaboni M, Delvarianzadeh M, Arabameri M (2021). Concentration and health risk assessment of polycyclic aromatic hydrocarbons in commercial tea and coffee samples marketed in Iran. *Environ Sci Pollut Res* 28:4827–4839. 0

Shariatifar N, Moazzen M, Arabameri M, Moazzen M, Khaniki GJ, Sadighara P (2021) Measurement of polycyclic aromatic hydrocarbons (PAHs) in edible mushrooms (raw, grilled and fried) using MSPE-GC/MS method: a risk assessment study. *Appl Biol Chem* 64:1–11.

Teimoori, S., Shirkhanloo, H., Hassani, A. H., Panahi, M., &Mansouri, N. (2023). New extraction of toluene from water samples based on nano-carbon structure before determination by gas chromatography. *International Journal of Environmental Science and Technology*, 20(6), 6589-6608.

Thamatam, N., Ahn, J., Chowdhury, M., Sharma, A., Gupta, P., Marr, L. C., ...&Agah, M. (2023). A MEMS-enabled portable gas chromatography injection system for trace analysis. *Analytica ChimicaActa,* 1261, 341209

Ugochukwu, U. C., & Ochonogor, A. (2018). Groundwater contamination by polycyclic aromatic hydrocarbon due to diesel spill from a telecom base station in a Nigerian City: assessment of human health risk exposure. *Environmental Monitoring and Assessment,* 190(4).

Ukaogo P.O., Loai A.b, Anthony O., Ojah E.O., Nwaogwugwu J.C. (2021), Evaluation of physicochemical characteristics and health risk of polycyclic aromatic hydrocarbons in borehole waters around automobile workshops in Southeastern Nigeria. Groundwater for Sustainable Development, 14 100615.