Edelweiss Applied Science and Technology
ISSN: 2576-8484
Vol. 8, No. 3, 368-373
2024
Publisher: Learning Gate
DOI: 10.55214/25768484.v8i3.1662

Estimation of levels of polycyclic aromatic hydrocarbons (PAHs) in the waters of Lake Habbaniyah in Anbar Governorate

Majeed Mahmoud AL-Duleimi[1]*, Reidh A. Abdul Jabar[2]
[1]Ministry of Education, Anbar, Iraq; aamkaq158@gmail.com (M.M.A.D)
[2]Department of Biology, College of Science, University of Tikrit, TiKrit, Iraq; dr.riedh@gmail.com (R.A.A.J).

Abstract: In this study, 16 polycyclic aromatic hydrocarbons (PAHs) were measured in the waters of Lake Habbaniyah, which are considered highly polluted materials. Three sites were selected in the heart of the lake, each site had two stations, the surface as one and the other at the bottom at a depth of four to five meters. The study lasted for 12 months from November 2022 to October 2023. The Level's PAHs were analyzed and measured by Gas Chromatography (GC). The study showed that the lake water contains only five PAHs, and that the tricyclic aromatic hydrocarbons were within the permissible limits, but the tetracyclic and pentacyclic compounds had exceeded the permissible limits. In this study, the ratio (LMH/HMW) was less than (1), indicating that the sources of PAHs in the lake It was mainly of thermal origin. Among the list of micropollutants noted for water quality pollution are the group (PAHs) [1]. PAHs are hazardous organic compounds that contain aromatic rings fused to their molecules [2]. These polynuclear compounds are a class of organic chemicals consisting of two or more condensed rings that can be distributed in particles, sediments and water columns and do not contain heterogeneous atoms or carry substituted groups [3].

Keywords: *Environment, Lake Habbaniyah, PAHs.*

1. Introduction

Many PAHs have toxic activities towards a variety of microorganisms and invertebrates [4]. PAHs have become a concern for ecosystems, health and carcinogenic properties, so many studies have focused on the environment polluted by PAHs [5]. One of the important properties of these compounds is the hydrophobic property and they are suspended in the water column or may settle in sediments, which causes a decrease in the level of their biological presence when the suspended matter increases and reduces their toxic risks to living organisms [6]. The sources of PAHs are waste and human wastes that are associated with thermal processes, incomplete combustion of organic matter or industrial activities accompanying incomplete combustion processes or during chemical manufacturing [7]. The physical and chemical properties of PAHs are often found as white, pale yellow or colorless solids, and their properties change with increasing molecular weight [8] and react with other pollutants such as chlorine, sulfur dioxide, ozone and nitrogen oxides to form dicyclic aromatic hydrocarbons (PAHs) [9]. PAHs can be divided into two main groups: the first group includes light or low molecular weight compounds with two or three fused benzene rings, ranging from naphthalene to fluorine. PAHs in this group are highly toxic to mammals. The second group includes PAHs with 4-6 fused benzene rings, ranging from chrysene to indeno-1,2,3-cyclopropene. Most PAHs are lipophilic, but some PAHs are soluble in water. However, they are highly volatile. On the other hand, PAHs with a large number of rings are insoluble in water and tend to adsorb strongly on particle surfaces, especially nonpolar particle

* Correspondence: aamkaq158@gmail.com

surfaces [10]. The resistance of PAHs to oxidation-reduction reactions increases with increasing molecular weight (Nikhavhamby et al.), and the The number of rings affects the range of boiling and melting points of PAHs and their fate in ecosystems depends on their physical and chemical properties [10]. Humans are exposed to these compounds through ingestion of contaminated food and water, skin contact, and direct inhalation of contaminated air [6].

2. Materials and Methods

2.1. Study Area and Samples

Three sites with six stations were selected, each operating two stations, one at the surface and one at a depth of four to five meter. The location of study on the surface were given the cods (1, 2, 3) and each the depths were given the numbers (4, 5, 6). The first site was south of the lake, which includes the first station and the fourth station, and is located at the coordinates (P1=E43.5185, N33.2742). The second site, which is located in the middle of the lake, includes the second and fifth stations, and is located at the coordinates (P2=E43.4470, N33.3004). The third site, which is located north of the previous site, includes the third and sixth stations at the coordinates (P3=E43.3963, N33.3264), noting that all sites and stations are located in the heart of the lake, several kilometers away from the coast. The selection of these sites and stations within Lake Habbaniyah came as a result of several reasons, including the lack of scientific studies and research, especially for the heart of the lake, especially with regard to productivity and PAHs, as most or all previous studies on the lake were within the coastal area only and did not reach the heart of the lake. In addition, these sites and stations were selected within the deeper areas of the lake, taking into account the nature of the area, the security aspect, and the possibility of reaching the stations during the study period, which lasted 12 months.

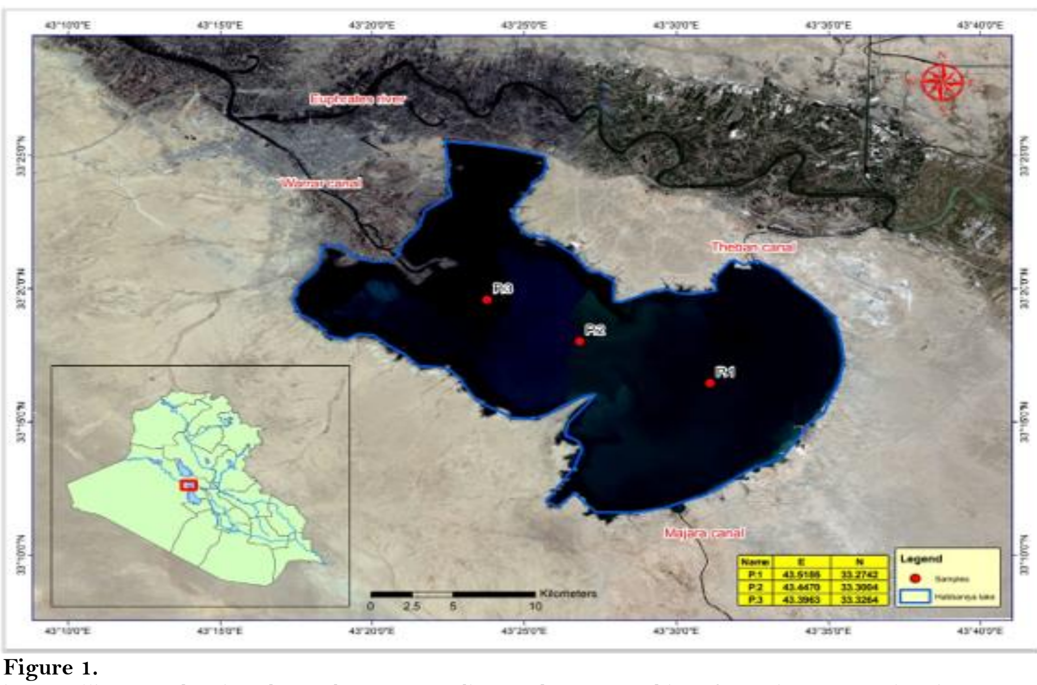


Figure 1.
is a satellite map showing the study area according to the Geographic Information System (GIS) program.

2.2. Sample Collection and Analysis

After cleaning the glass and plastic tools used by washing them with water and cleaning powders, and sometimes we need to sterilize them, then wash them with distilled water, then dry them in the oven. Samples were collected from the lake at its three sites and six stations at a rate of one sample per

ISSN: 2576-8484
Vol. 8, No. 3: 368-373, 2024
DOI: 10.55214/25768484.v8i3.1662

month during the study period, which lasted 12 months, starting from November 25, 2022 until October 25, 2023, the study samples were collected from the layers close to the surface, about thirty centimeters deep, for ten minutes. The samples were divided into two parts, the first from the surface and the second from the bottom, at various distances. The first was at a depth of four to five meters. The samples were collected using a 2.5-liter polyethylene container after washing it twice with sample water at each station using a Phantom (CG) device.

2.3 Measurement of the Concentration of Aromatic Cyclic Hydrocarbons

Using Whatman filter paper (70 mm) to remove suspended solids, 800 ml of water samples were taken and reconcentrated to a final volume of 2 ml with appropriate levels of N and analyzed by GC/FID. After feeding into a 500 ml mesh, soxhite extraction was carried out. For detection of polycyclic aromatic hydrocarbons (PAHs), 20 ml of normal hexane and dichloromethane (90: (v/v) respectively and 10)) (v/v) mixture (30 ml) were added and PAHs of the following 16 compounds were detected.

3. Results and Discussion

The activity of human civilization and development and progress in all areas of life, especially in the field of industry, has caused the release of pollutants into the environment. Water pollution is associated with human activities, which represent a major source of PAHs. PAHs are often not found separately in the aquatic environment, so they are viewed as a mixture. The total concentration of the mixture is used to describe the amount of these compounds [11]. In this study, we used the (GC) technique to measure the levels of PAHs in water samples. In this study, (16) compounds were measured. Only five compounds were obtained in lake samples, which are (Fluorene, Chrysene, Benzo(a) Pyren, Benzo(a) Fluranthen, Benzo(a,h) Anthracene).There are (11) compounds whose result was (ND) because the device did not sense their concentrations, although it measures concentrations at a rate of (pbb). The five-ring PAHs (5 Ring) were the most abundant in the study, as their percentage was (65.87%), followed by the PAHs (3 Ring) at a rate of (17.30%), and finally came the PAHs (4 Ring) by (16.82%) and thus the lake was free of di- and hexa-ring compounds. High molecular weight PAHs (HMW) prevailed, reaching (55.62%), while low molecular weight PAHs (LMW) reached (44.37%).

Table 1.
Concentrations of PAHs (µg/L) in the waters of Lake Habbaniyah at the studied stations.

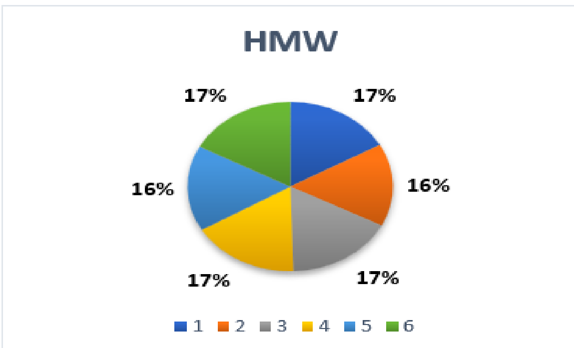
Elements	S. 1		S. 2		S. 3		S. 4		S. 5		S. 6	
	Mean	Range	M	R	M	R	M	R	M	R	M	R
Flu.	19.99	15.5-28.6	19.9	18.6-24.9	21.8	16.6-36.6	20.3	16.9-25.9	21.3	15.8-25.7	21.4	15.9-28.9
Chr.	20.33	13.8-27	20.7	13.6-26.8	19.8	13.55-27.5	19.4	12.5-28.6	19.6	12.9-27.2	21.2	12.9-26.9
B. (a) pyr.	0.131	0.051-0.251	0.155	0.075-0.455	0.235	0.085-0.645	0.265	0.085-0.525	0.245	0.045-0.085	0.212	0.065-0.456
B. (a) flu.	24.11	16.9-37.9	23.25	17.55-38.9	25.7	17.85-39.55	26.05	17.2-37.9	26.25	16.8-38.8	26.25	17.7-36.8
B. (ah) Ant.	60	50.8-69.7	54.2	51.4-68.5	59.6	50.8-69.8	59.8	50.9-69.7	55.6	50.8-69.5	59.2	51.4-68.9

Petroleum-based pollution is characterized by a high proportion of low-molecular-weight (LMW) polycyclic hydrocarbons with two or three aromatic rings, while high-molecular-weight (HMW) polycyclic hydrocarbons with four, five, or six rings are of thermal origin [6].

Table 2.
Average ratios (LMW/HMW) of PAHs in water samples at the studied stations.

Station. No.	L.M.W.	H.M.W.	L.M.H./H.M.W.	Origine
ONE	19.8	26.2	0.755	Pyrogenic
TWO	19.9	24.6	0.808	Pyrogenic
THREE	21.8	26.3	0.828	Pyrogenic
FOUR	20.3	26.4	0.768	Pyrogenic
FIVE	21.3	25.4	0.838	Pyrogenic
SIX	21.4	26.7	0.801	Pyrogenic

The PAH/PAH ratios shown in Table 2 are less than 1, indicating that the source of PAHs in the lake is mainly thermal.



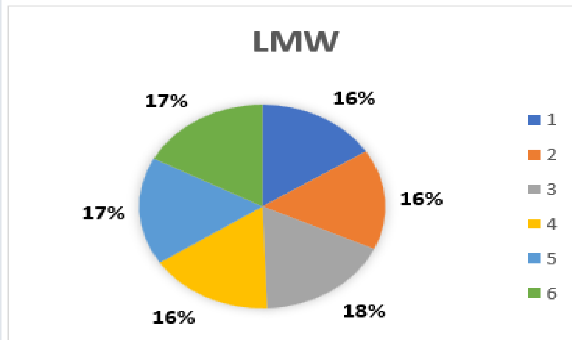


Figure 1.
The percentage of PAHs in water samples of the Habbaniyah Lake sites during the study period according to the number of episodes for each station.

3.1. Fluorene

The highest value of fluorine was recorded during the month of February at the third station, where it reached (36.5 µg/L), and the lowest value was recorded in June at the first station, where it reached (15.4 µg/L). We can attribute the increase to the rains during the winter season, which bring fluorine from the air or from the lands adjacent to the lake, as fluorine is often produced by engines, gas turbines, diesel, gasoline and kerosene engines, coke ovens and stoves. [12].

3.2. Chrysene

A compound consisting of four benzene rings that can be obtained in wastewater from petrochemical, metallurgy, plastics and paint industries. The biodegradability of chrysin by living organisms is slow, in addition to that it has a tendency to accumulate in aquatic organisms such as fish [13]. The value of (MAC-EQS) is 19 pbb for all water bodies, so some stations exceeded this value as shown in Table (1). The results of the study showed that the highest value of chrysin was (28.5 µg/L) during September at the fourth station and the lowest concentration was (12.4 µg/L) in April at the same station. The reason for the increase may be that high molecular weight compounds HMW - PAHs are less volatile in the environment and get adsorbed on soot particles formed during incomplete combustion and thus are less susceptible to breakage [14]. Also, solubility decreases with increasing number of rings in the compound, as the relationship is inverse between solubility and number of rings [15]. As for the decrease in concentrations in the spring, it is explained that the increased exposure of PAHs to light makes them more susceptible to fragmentation processes in their chemical composition, forming new compounds that differ in physical and chemical properties such as oxygen, ultraviolet rays, and solar radiation [16].

3.3. Benzo [A] Pyrenen

PAHs contain five fused benzene rings. Benzo(a)pyrene is a highly toxic, mutagenic and carcinogenic pollutant, and is classified by the World Health Organization as a probable human carcinogen [17]. The role of chlorophyll in the photodegradation of benzo(a)pyrene is very important, as it could be a strategy for cleaning up organic pollutants in aquatic environments. Dead algal cells may act as photosensitizers and promote the photodegradation of PAHs [18]. Table (1) shows that the highest values of benzo(a)pyrene were found in September at 0.82 μg/L, and the lowest value was 0.04 μg/L.during December at the same station (Station 5). The increase in the concentration of the compound could be attributed to the decrease in water levels in the lake or to the amount of emissions from car exhausts and the discharge of household and health waste directly into the lake or into the Warar Canal. It could also be due to the geology of the area, environmental conditions, the nature of aquatic ecosystems and the method of analyzing the compounds. All of these are considered influential factors [19]. As for the reason for the decrease, The concentrations of Benzo(a)pyrenene compound can be attributed to the presence of aquatic plants that play an important role in removing PAHs from water through absorption and accumulation [20]. The levels of Benzo(a)pyrenene compound were higher than the permissible limits according to (MAC-EQS) which amounted to (0.27 pbb).

3.4. Benzo [a] Fluranthene

From Table (1), we note that the highest value of the compound Benzo (a) Fluranthene was in September and at the third station, where it reached (39.5 μg/L), and the lowest value was (16.8 μg/L) at the second station during the month of November. The reason for the increase in the percentages of the above compound is due to the nature of the water and the amount of organic materials present, as the lake and the Warar Canal are located within or pass through agricultural areas and areas for grazing sheep and cattle, so sheep and cattle waste may increase the organic materials containing the compound Benzo (a) Fluranthene, in addition to the fact that it may be present in sewage waste, as this compound exceeds the permissible limits according to [2], which amount to 5 pbb.

3.5. Dibenzo [a,h] Anthracene

An aromatic cyclic compound, soluble in organic solvents such as petroleum ether, industrial ethers, dyes and benzene, but insoluble in aqueous solvents. Highly adsorbent to sediments and particles. When discharged into water, it evaporates without decomposition. It also shows some bioaccumulation in aquatic organisms without microsomal oxidase [21]. The highest value of (A,H) anthracenide benzo-p-dioxin was at station 3 in September (69.8 μg/L), the lowest at stations 3 and 5 in November and the lowest at station 1 in December (50.8 μg/L). This compound exceeded the permissible limit according to [2], which is 5 parts per billion.

4. Conclusions

1- The lake water is exposed to many external influences such as low water levels due to drought and lack of rain, in addition to its interference with human activities, which has affected all environmental factors of the lake water and affected biological communities, including algae, which are considered the main producer in the lake water. 2- In this study, (16) compounds measured. Only five compounds were obtained in lake samples.

2- Tricyclic aromatic hydrocarbons were within the permissible limits, but the tetracyclic and pentacyclic compounds had exceeded the permissible limits.

3- In this study, the ratio (LMH/HMW) was less than (1), indicating that the sources of PAHs in the lake were mainly of thermal origin.

References

[1] E. R. Christensen and S. Arora, "Source apportionment of PAHs in sediments using factor analysis by time records: Application to Lake Michigan, USA," *Water Res.*, vol. 41, no. 1, pp. 168–176, 2007, doi: 10.1016/j.watres.2006.09.009.

[2] U. S. D. of H. and H. Services, "Agency for Toxic Substances and Disease Registry-ATSDR.," 2017.

[3] H. I. Abdel-Shafy and M. S. M. Mansour, "A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation," *Egypt. J. Pet.*, vol. 25, no. 1, pp. 107–123, 2016, doi: 10.1016/j.ejpe.2015.03.011.

[4] M. Schloter, O. Dilly, and J. C. Munch, "Indicators for evaluating soil quality," *Agric. Ecosyst. & Environ.*, vol. 98, no. 1–3, pp. 255–262, 2003, doi: 10.1016/s0167-8809(03)00085-9.

[5] H.-H. Liste and I. Prutz, "Plant performance, dioxygenase-expressing rhizosphere bacteria, and biodegradation of weathered hydrocarbons in contaminated soil," *Chemosphere*, vol. 62, no. 9, pp. 1411–1420, 2006, doi: 10.1016/j.chemosphere.2005.05.018.

[6] M. Honda and N. Suzuki, "Toxicities of Polycyclic Aromatic Hydrocarbons for Aquatic Animals," *Int. J. Environ. Res. Public Health*, vol. 17, no. 4, p. 1363, Feb. 2020, doi: 10.3390/ijerph17041363.

[7] Y. Lin, X. Qiu, Y. Ma, J. Ma, M. Zheng, and M. Shao, "Concentrations and spatial distribution of polycyclic aromatic hydrocarbons (PAHs) and nitrated PAHs (NPAHs) in the atmosphere of North China, and the transformation from PAHs to NPAHs," *Environ. Pollut.*, vol. 196, pp. 164–170, 2015, doi: 10.1016/j.envpol.2014.10.005.

[8] A. Malakahmad, T. S. B. A. Manan, S. Sivapalan, and T. Khan, "Genotoxicity assessment of raw and treated water samples using Allium cepa assay: evidence from Perak River, Malaysia," *Environ. Sci. Pollut. Res.*, vol. 25, pp. 5421–5436, 2018.

[9] P. Wang, H. Shen, and P. Xie, "Can Hydrodynamics Change Phosphorus Strategies of Diatoms?—Nutrient Levels and Diatom Blooms in Lotic and Lentic Ecosystems," *Microb. Ecol.*, vol. 63, no. 2, pp. 369–382, 2011, doi: 10.1007/s00248-011-9917-5.

[10] A. Buha and M. Williams, "Polycyclic aromatic hydrocarbons," *Retrieved Oct.*, vol. 27, p. 2016, 2011.

[11] J. Helfrich and D. E. Armstrong, "Polycyclic aromatic hydrocarbons in sediments of the southern basin of Lake Michigan," *J. Great Lakes Res.*, vol. 12, no. 3, pp. 192–199, 1986.

[12] H. Al-Saad, W. Farid, and W. Abdul-Ameer, "Distribution and sources of polycyclic aromatic hydrocarbons in soils along the Shatt Al-Arab River Delta in southern Iraq," *Soil Water Res.*, vol. 14, no. 2, pp. 84–93, 2019, doi: 10.17221/38/2018-swr.

[13] S. Biswas and B. Ghosh, "Chrysene," *Encyclopedia of Toxicology*. Elsevier, pp. 959–962, 2014. doi: 10.1016/b978-0-12-386454-3.00286-4.

[14] L. Staffan, "Analysis of PAHs and their transformation products in contaminated soil and remedial process," *Sweden Sofjadern Offset AB*, 2003.

[15] D. Mackay, W. Y. Shiu, and K. C. Ma, *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals-Volume IV: Oxygen, Nitrogen, and Sulfur Containing Compounds*. 1995.

[16] P. D. Monson, G. T. Ankley, and P. A. Kosian, "Phototoxic response of *Lumbriculus variegatus* to sediments contaminated by polycyclic aromatic hydrocarbons," *Environ. Toxicol. Chem.*, vol. 14, no. 5, pp. 891–894, 1995, doi: 10.1002/etc.5620140522.

[17] F. Lyon, "IARC monographs on the evaluation of carcinogenic risks to humans," *World Heal. Organ. Int. agency Res. cancer. availble Publ. iarc. fr*, 2014.

[18] L. Luo, P. Wang, L. Lin, T. Luan, L. Ke, and N. F. Y. Tam, "Removal and transformation of high molecular weight polycyclic aromatic hydrocarbons in water by live and dead microalgae," *Process Biochem.*, vol. 49, no. 10, pp. 1723–1732, 2014, doi: 10.1016/j.procbio.2014.06.026.

[19] T. F. da Silva, D. de A. Azevedo, and F. R. de Aquino Neto, "Distribution of polycyclic aromatic hydrocarbons in surface sediments and waters from Guanabara Bay, Rio de Janeiro, Brazil," *J. Braz. Chem. Soc.*, vol. 18, no. 3, pp. 628–637, 2007, doi: 10.1590/s0103-50532007000300021.

[20] S. Hsu, "Removal polycyclic aromatic hydrocarbons (phenanthrene and pyrene) in aquatic phase by Ceratophyllum demersum and Naja gramunea," 2005.

[21] T. J. Nekhavhambe, T. Van Ree, and O. S. Fatoki, "Determination and distribution of polycyclic aromatic hydrocarbons in rivers, surface runoff, and sediments in and around Thohoyandou, Limpopo Province, South Africa," *Water SA*, vol. 40, no. 3, p. 415, 2014, doi: 10.4314/wsa.v40i3.4.