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Article

Detection of Polycyclic aromatic hydrocarbons in Hawija Irrigation Project, Kirkuk

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Abstract: This study investigates the presence of polycyclic aromatic hydrocarbons (PAHs) in the waters of the Hawija Irrigation Project, Kirkuk, Iraq. The research aims to assess the concentrations of PAHs across five sampling sites over six months, analyzing environmental and seasonal variations. Samples were collected bi-monthly from December 2023 to May 2024, with PAH concentrations determined using GC-MAS. Results show significant variations in PAH levels among sites and months. The second site exhibited the highest concentrations, particularly for Benzo[k]fluoranthene (21.58±28.3 μg/L) and total PAHs (31.63±33.7 μg/L), while the fourth site had the lowest levels (12.24±14.9 μg/L). Seasonal trends revealed higher concentrations during winter, attributed to increased fuel combustion and atmospheric deposition. However, all recorded concentrations remained within permissible limits. This study highlights the importance of monitoring PAHs to ensure water quality and mitigate potential ecological impacts, emphasizing the need for sustainable management of water resources in the region.

Keywords: PAHs; Water Quality; Naphthalene; GC-MAS.

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1. Introduction

The disruptions in ecosystem sustainability, particularly the overuse of water resources, have a negative impact on society and people's means of subsistence. The availability of resources, economic development, and social features can all be impacted by changes to one of our ecosystems' constituent parts. Within the constraints of the environmental resources at hand, humanity requires effective leadership through sustainable activities [1]. Human life and other living things are at danger due to the issue of water pollution. Over time, this issue has arisen as a result of both population growth and industrial advancement. Due to inadequate planning and planned use of environmental resources, this issue has grown to be one of the most significant worldwide issues [2]. Many pollutants' levels of danger are determined by their chemical makeup, level, and distribution across water, air, land, and living organisms. The level of the pollutant can be fixed as the pollutant itself, suspended in water, or linked to dust particles. Since surface water is regarded as a freshwater reservoir and is one of the main sources of water for drinking in many nations worldwide, it is subject to a wide range of contaminants, including those from urban and agricultural processes, which are currently a major global issue [3]. Multiple rings fused together without atoms or substituents are known as PAHs [4]. Since PAHs are highly stable [5–6] and can build up in fatty tissues in the food chain, they are categorized as significant environmental contaminants. Low molecular weight PAHs also have a hazardous equivalency factor, whereas high molecular weight PAHs, including B[a]py, exhibit mutagenic and carcinogenic effects [7-8]. Both natural and man-made processes release PAHs into the environment, mostly through incomplete burning of fossil fuels including coal and petroleum in power plant operations, vehicle emissions, and home heating [2–3]. Therefore, the current study aims to detection of PAHs in Hawija Irrigation Project.

2. Materials and Methods

Study Area

Tigris River

The Tigris River is one of the most important rivers in Iraq, as it originates from the highlands of southeastern Turkey and its length from its source to its mouth is 1718 km, 1418 km of which is its course within Iraqi territory. Thus, Iraq has a share of the area and length of the Tigris basin that is more than several times its area and length in Turkey and Syria [9]. Large tributaries spread across Iraq, Turkey and Iran flow into the river, the most important of which are the Khabur, the Great Zab, the Little Zab, the Great Zab and the Diyala River.

Al-Hawija irrigation project

Al-Hawija irrigation project (fig: 1) is located in Al-Hawija district, Kirkuk Governorate, located (70) km southwest of Kirkuk city, on the left side of the Lower Zab River, bordered on the west by Al-Abbasi district and on the east by Riyadh district, and is located between latitudes (35°,38.55) and (35°,51.30) north, and longitudes (43°,56.30) and (43°,38.30) east. One of the primary sources of surface water in the Al-Hawija district is the Al-Hawija irrigation project. The study stations were chosen for a number of reasons, such as the dearth of environmental investigations and studies on the area, the absence of information elucidating the environmental characteristics of the project water and the degree of environmental contamination in it, the characteristics of the area, and the potential for selecting the most appropriate study station locations while accounting for the direct impacts of population centers in these stations.

Al-Huwayjah Irrigation Project Samples

Samples were collected from Al-Huwayjah Irrigation Project at a distance of (4-5) meters from the bank and at a depth of not less than (30) centimeters. The sample collection process starts from eight in the morning until two in the afternoon at a rate of twice a month (beginning of the month and middle of the month). Sample collection started from December 2023 until May 2024. Water samples were collected in sterile glass bottles containing one liter of water to which 20 ml of n-hexan was added. The mixture was shaken for an hour and then the solvent was extracted.

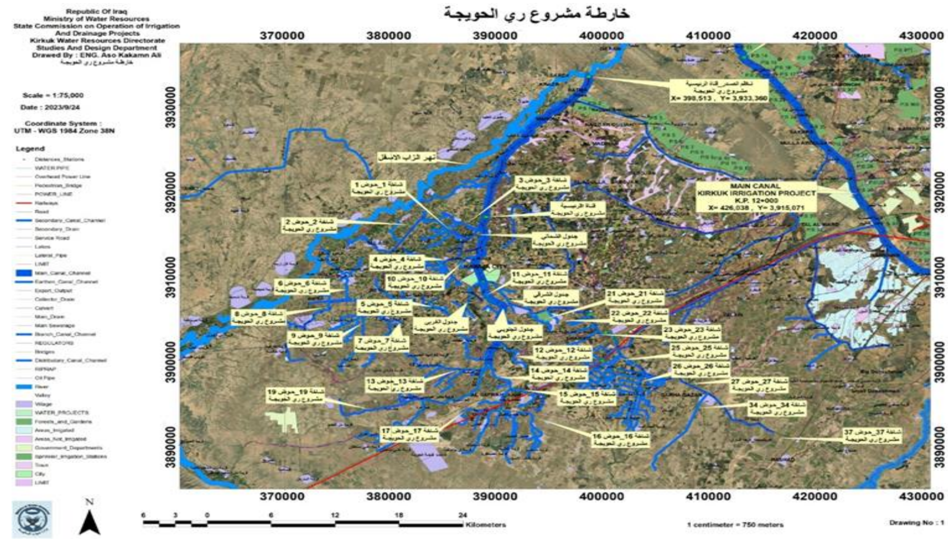

Figure (1): Hawija Irrigation Project Map.

Extraction of Polycyclic aromatic hydrocarbons from water

The extraction of PAHs from river water is a complex process that requires a series of chemical and physical steps. This process is used in the analysis of water samples to determine the presence and concentration of these compounds that may be environmental pollutants. A sample of river water is collected in a clean, dry glass container. A certain volume of carbon tetrachloride is added to the water sample. The sample is shaken well to ensure the distribution of PAHs between the organic phase (carbon tetrachloride) and the aqueous phase. The analysis is then carried out by GC-MAS.

3. Results and Discussion

Table (1) shows the naphthalene values in the different study sites during the six months. The highest naphthalene rate was in the second site during the study months, reaching (2.835±3.52), while the third site had the lowest naphthalene levels during the study months, reaching (0.05±0.13), and non-significant differences were observed (P<0.05) between the months in the third site. On the other hand, with regard to the naphthalene values during the study months, the highest naphthalene value was in May, reaching (1.818±4.07), and significant changes were observed (P<0.05) between the sites in this month, while the lowest naphthalene value was in April, reaching (0.0±0.0), (table 3).

Table (2) shows the values of Benzo[k]fluoranthene in the different study sites during the six months. The highest Benzo[k]fluoranthene rate was in the second site during the study months, reaching (21.58±28.3), while the first site had the lowest Benzo[k]fluoranthene levels during the study months, reaching (8.02±8.21), and significant changes were observed (P<0.05) between the months in the first site. On the other hand, regarding the values of Benzo[k]fluoranthene during the study months, the highest Benzo[k]fluoranthene value was in March, reaching (34.28±21.4), and non-significant changes were observed (P<0.05) between the sites in this month, while the lowest Benzo[k]fluoranthene value was in January, reaching (0.97±2.17), (table 3).

Table (2) shows the values of total PAHs in the different study sites during the six months. The highest rate of total PAHs was in the second site during the study months, reaching (31.63±33.7), while the fourth site had the lowest levels of total PAHs during the study months, reaching (12.24±14.9), and significant changes were observed (P<0.05) between the months in the fourth site. On the other hand, with regard to the values of total PAHs during the study months, the highest value of total PAHs was in May, reaching (43.54±21.6), and non-significant changes were observed (P<0.05) between the sites in this month, while the lowest value of total PAHs was in January, reaching (3.06±2.72), (table 3).

Table (2) shows the average of some PAHs of the study samples according to the site.

Site / Parameters	1	2	3	4	5
Naphthalene	0.91±1.56 a	2.835±3.52 a	0.05±0.13 a	0.11±0.21 a	0.28±0.68 a
Benzo[k]fluoranthene	8.02±8.21 a	21.58±28.3 a	11.79±12.7 a	9.22±10.8 a	11.92±18.6 a
Total polycyclic aromatic hydrocarbons	22.41±15.2 a	31.63±33.7 a	24.58±26.4 a	12.24±14.9 a	21.43±28.9 a

Table (3) shows the average of some PAHs of the study samples according to the study months, and non-significant changes were observed in the properties between the study months.

Table (3) shows the average of some PAHs of the study samples according to the study months

Site / Parameters	December	January	February	March	April	May
Naphthalene	1.48±2.03 a	0.845±1.63 a	0.548±0.68 a	0.332±0.74 a	0.0±0.0	1.818±4.07 a
Benzo[k]fluoranthene	1.93±3.16 a	0.97±2.17 a	1.56±3.48 a	34.28±21.4 a	7.12±7.39 a	29.17±8.53
Total polycyclic aromatic hydrocarbons	26.34±30.6 a	3.06±2.72 a	7.53±11.3 a	42.27±23.0 a	12.02±13.4 a	43.54±21.6 a

Analysis of variance and Duncan's test documented significant differences between naphthalene means at a significant level ($P \geq 0.05$) relative to the sampling sites, while significant differences were recorded relative to the sampling months. The correlation coefficient was negative between naphthalene value and temperature ($r = -0.393$), the correlation coefficient was positive between naphthalene value and turbidity ($r = -0.0109$), the correlation coefficient was negative between naphthalene value and electrical conductivity ($r = -0.0657$), the correlation coefficient was positive between naphthalene value and total solids ($r = 0.1071$), while the correlation coefficient recorded a negative correlation between naphthalene value and pH ($r = -0.8871$), the correlation coefficient recorded a positive correlation between naphthalene value and dissolved oxygen ($r = 0.1696$), while the correlation coefficient recorded a positive correlation between naphthalene value and and nitrates ($r= 0.7139$), while the correlation coefficient recorded a zero correlation between the value of naphthalene and phosphate ($r= 0.000$), while the correlation coefficient recorded a positive correlation between the value of naphthalene and sulphates ($r= 0.5611$).

The contents of PAHs in water were shown to be negatively correlated with temperature. Since high temperatures cause PAHs to evaporate from water, the summertime concentration drop could be caused by high temperatures [10]. Additionally, high temperatures encourage microbes to break down these substances, particularly those with small molecular weights [11]. The length of the day and the strength of the sun's rays cause the photo-oxidation process to be more intense [12]. However, the increased burning of fuel and wood for heating during the winter is the reason for the rise in concentrations of PAHS [13]. The results of PAHs were within the permissible limits: 100 ng/L [14]. Anthropogenic activities are the primary source of PAHs in the aquatic environment, accounting for a larger portion of environmental contamination than sources from nature [15]. In addition to rain and the pollutants and odors it delivers from cities, the primary source of PAHs in the aquatic environment is precipitation from the atmosphere in the form of particulate matter from the burning of coal and fuel [16]. As is clear from the results of the current study, Naphthalene and Benzo[k]fluoranthene compounds are recorded as the most abundant and concentrated PAHs, due to the lipophilic nature of these compounds and their low solubility in water [17]. Their presence suggests the use of petroleum derivatives for boat engines, precipitation or deposition from the atmosphere, as well as wastewater from cities [18]. Dickhut et al. [19] confirmed that aromatic compounds with the same molecular weight have similar dynamics in their transport in the aquatic environment. During this investigation, the PAH concentrations at sites 4 and 2 varied from 0.15 to 75.76, respectively. The reduced water volume and flow rate at site 2 might be the cause of the higher concentrations there; this trend is comparable to that seen in the Hilla River [20]. Furthermore, the combined impact of PAH emissions from vehicle exhausts and sediment release may be the cause of the increased amounts in the water samples at site 2 [21–22]. The current study's values were less than those found by Al-Azawey et al. [24] in the Hilla River and Mohammed et al. [23] in the Euphrates River.

Low water levels, which expose the river directly to air and land pollutants that dissolve in the river water, as well as the amount of traffic and possible human activity on both banks of the river were all linked to PAHs in the Lower Zab and Tigris Rivers [25–26]. Additionally, diesel may leak straight into the river water due to the usage of diesel pumps for irrigation of agricultural regions along the river. Generally speaking, a lack of environmental education and awareness leads to the frequent disposal of petroleum products into rivers. Numerous studies link agricultural practices, untreated sewage discharge, exhaust from cars, and industrial and municipal wastes that directly dump PAHs into rivers with aquatic pollution [25, 27]. The majority of PAH concentrations that have been measured have been found to be below the advised levels [28]. Al-Saad [10] demonstrated that a plausible explanation for the wintertime concentrations could be that, because of more extensive combustion and a stronger correlation between these hydrocarbons and air particles at lower ambient temperatures, total hydrocarbon discharges were higher than during the summer. Additionally, summertime petroleum hydrocarbon deposits on land would not have the same impact on the aquatic environment as wintertime runoff from land, when the area experiences more frequent rainstorms.

4. Conclusion

It was concluded from the current study that the concentration of Polycyclic aromatic hydrocarbons did not exceed the permissible limits in the waters of the Hawija irrigation project, and that winter is the season in which the levels of PAHs rise the most.

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