



Environmental Study of Some Polycyclic Aromatic Hydrocarbons in Edku Wetland Waters, Egypt

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ABSTRACT

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Edku Wetland is considered one of the most important lakes in northern Egypt. Sixteen polycyclic aromatic hydrocarbons (PAHs) in eight water samples were studied during the spring and summer of 2022 to determine the spatial and seasonal distribution, source of PAHs, toxicity, and ecological risk for the lake water. PAHs were analyzed using gas chromatography. The concentration of Σ 16PAHs recorded the lowest values of 115.80 and 54.80ng/ L, which represents the sea-lake contact point during spring and summer, and the highest values of 210.60 and 182.10ng/ L during the same seasons, respectively, which represents the main connection point of the drainage lake. The PAH composition pattern by ring type showed a considerable predominance of the three-ring, four-ring, and six-ring PAHs. To evaluate the possible sources of PAHs, the molecular indices were determined by the calculation of Σ LMW/ Σ HMW, Benzo(a)anthracene/ Chrysene BaA/ (BaA/ Chry), Indeno (1,2, cd) pyrene/ Benzo(g) (In/ BgP), Phenanthrene/Anthracene (Phe/ Ant), and Fluoranthene/Pyrene (Flua/ Pyr) ratios. The results indicate that the significant source of PAHs in the water lake was a pyrogenic source, resulting from the combustion of fuel, wood, and grasses. The toxicity and ecological risk assessment indicates that there were no observed hazard to the environment. Risk quotients suggested the safety of the lake water from the possibility of cancer for BaP toxic equivalents, and incremental lifetime cancer risk being very low.

INTRODUCTION

Edku Wetland is considered one of the coastal lakes of the northern Egyptian Delta, which is directly connected to the Mediterranean Sea (Moneer *et al.*, 2022). Moreover, it is considered the third largest northern Egyptian coastal lake in the Nile Delta, located in the Beheira Governorate, and one of the most threatened aquatic environments in Egypt due to anthropogenic activities and pollution (Mehanna, 2009). Polycyclic aromatic hydrocarbons (PAHs) are organic compounds consisting of two or more fused aromatic rings and can also be referred to as polynuclear aromatic hydrocarbons (PNAs), fused ring aromatics, or condensed ring aromatics (Akintelu *et al.*, 2018; Reizer *et al.*, 2022). PAHs are semi-volatile, semi-soluble in water,

lipophilic, nonpolar, and colorless (Patel *et al.*, 2020). These compounds are not released into the environment as single compounds, hence PAHs are adsorbed on particles in the air, soil, water, and sediment (Ramesh *et al.*, 2012; Gao *et al.*, 2021). PAHs are formed mostly as a result of pyrolytic (devolatilization) processes, especially the incomplete combustion of organic materials during industrial and other human activities (Menichini & Bocca, 2003). The US Environmental Agency has identified 16 compounds of PAHs that must be monitored continuously in various environments. These compounds are of paramount importance in the occurrence of an environmental impact (mutagenic, toxic, or carcinogenic) and have a serious environmental threat (Bisht *et al.*, 2015; Inobeme *et al.*, 2023). The source of PAHs in the environment may be pyrogenic, resulting from the combustion of fossil fuels and contemporary carbon sources, which are recognized by their higher molecular weight. Additionally, petrogenic sources, such as uncombusted petroleum introduced to the water environment by an oil spill, contribute to PAH contamination. Natural non-combustion sources are another source for PAHs that result from degradation (Simcik & Offenber, 2006). Polycyclic aromatic hydrocarbons (PAHs) are compounds known to be carcinogenic that are produced from incomplete combustion of carbon-containing fuels, such as tobacco, wood, grease, coal, diesel, for example, incinerators, engines, and burns of forest biomass that can form or bind with tiny particles in the atmosphere (Murray & Penning, 2018). The danger of PAHs in the aquatic environment lies in their ability to accumulate in the food chain by biomagnification until they reach the human body, making them capable of poisoning due to their bioaccumulative characteristic (Law *et al.*, 2002). The purpose of the research was to study PAHs in the water of Edku Wetland in an attempt to trace the sources of pollution and preserve the lake water.

MATERIALS AND METHODS

1. Study area and sampling

The lake under study (Edku Wetland) is approximately 35km from Alexandria Governorate and west of the Nile River between longitudes of 30.17 and 30.23 E and latitudes of 31.23 and 31.27 N (Gu *et al.*, 2013; Ahmed, 2023). The lake water contains 90% of the water from the drains in addition to 10% of the seawater, especially the water of Abu Qir Bay through Boughaz El-Maadia, which is the connection point of the lake with the sea (El-Said *et al.*, 2021; Ahmed, 2023). Regarding drain water, which contains a large proportion of wastewater, industrial, agricultural, and domestic effluents flowing into the Kharity drain, it is connected to three drains and sub-channels: Damanhour Drain, Edku drain, and Al-Busaily drain. Additionally, there is the Barzeq drain located on the southern side of the lake and the content of agricultural wastewater (Hassan *et al.*, 2017).

The study area was divided into three locations with eight stations: the southern location containing Stations I, II, III, and IV, which are considered connecting locations of main drains with the lake, and the northern location containing Stations V, VI, and VII. The stations are located near the international road, the middle of the lake, and the area near Bugaz; finally, station

VIII, where the lake connects to the Mediterranean Sea, as illustrated in Fig. (1). A total of eight surface water samples were collected during spring and summer 2022 for the determination of PAHs in water samples. The surface water samples were collected from Edku Wetland using an amber glass bottle (2.5L). Before sampling, nitric acid (10%) was used to wash the bottle, followed by diluted and deionized water. The bottle was finally rinsed with water samples before collection to prevent cross-contamination during the process (Salaudeen *et al.*, 2018; Ambade *et al.*, 2021). Samples were preserved, kept in the icebox, and transferred to the laboratory. Water samples were stored in the refrigerator at -3°C for further analysis.

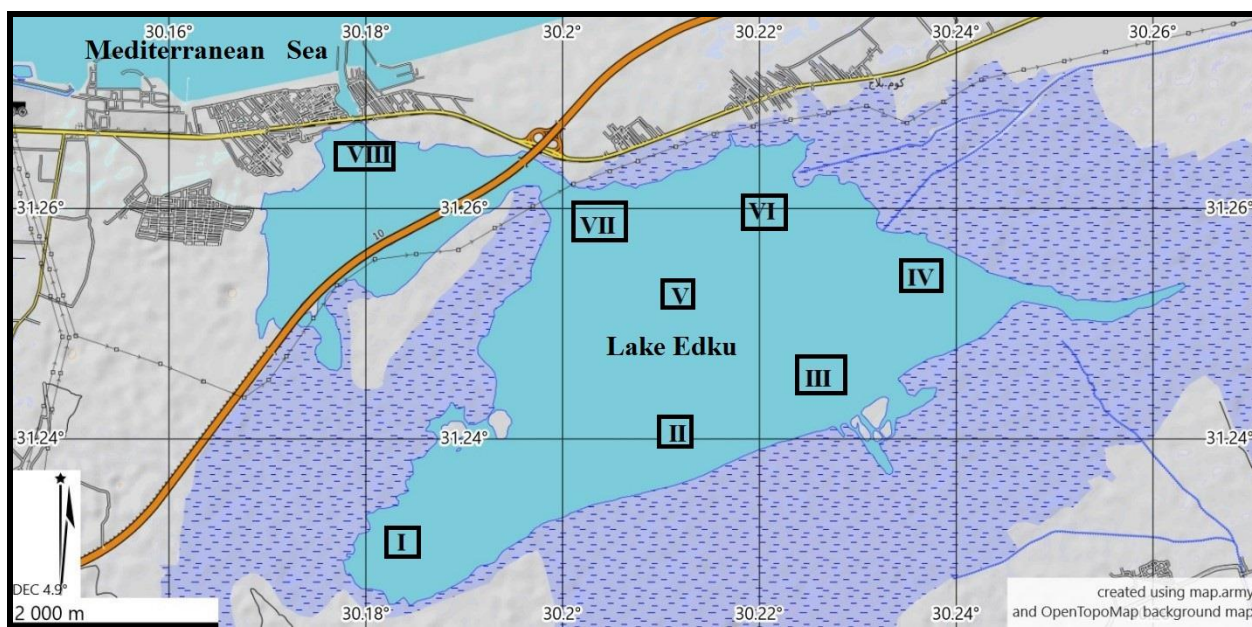


Fig. 1. A map showing the locations of water samples from Edku Wetland during study period

2. Sample extraction and preparation for analysis

Water samples were extracted through liquid-liquid extraction, followed by gas chromatographic analysis according to USEPA (1980) and Gómez-Gutiérrez *et al.* (2007). Samples were filtered through GF/F 45mm filter paper. One liter of each filtered water sample was mixed with 200mL of dichloromethane (DCM) and shaken vigorously for 5 minutes in a 5L conical flask, and then separated in a separating funnel. The lower layer of the organic solvent containing pollutants was collected on anhydrous Na_2SO_4 and pentachlorobenzene as an internal standard for organic chlorinate. The extract was concentrated by rotary evaporation to 2ml and then to 1ml under a gentle stream of pure N_2 .

3. Instrumental analysis

PAHs in water samples were analyzed by gas chromatography combined with the Flame Ionization Detector (GC-ECD; Chromatograph HP5890 II FID/ECD). For PAHs GC setting, flow pressure was 77.0kPa, detector temperature was 310°C , initial oven temperature was 50°C , final

temperature was 320°C, and injector temperature was 250°C. Moreover, the n-hexane solvent blank was first injected into the equipment, and its chromatogram was obtained. A 50m long column with a diameter of 0.25mm and a film thickness of 0.25µm was used. Standard injections were performed followed by sample injections (UNEP, 1992).

4. Quality assurance/ quality control

PAHs were quantified using a stock solution: benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, pyrene, benzo(a)pyrene, dibenzo (a, h) anthracene, benzo(ghi)perylene, and indeno (1,2,3-cd) pyrene. These PAHs were then diluted to create a series of calibration standards at 0.1, 0.25, 0.5, 0.75, 1.0, 2.0, 5.0, and 10µg/ ml. Three analyses were conducted on PAHs standard reference materials to study the recovery efficiency, which ranged from 50 to 102.1%. With a coefficient of variation ranging from 6.9 to 10.2% for all studied PAHs, analyzing blank samples spiked with a known quantity of each PAH standard used for quality assurance checks, the values of PAHs in the blank samples were below the detection limit of the instrument.

RESULTS AND DISCUSSION

As illustrated in Table (1) and Figs. (2, 3), the summation polycyclic aromatic hydrocarbons (Σ 16PAHs) range between 115.80ng/ L at station VIII and 210.60ng/ L at station II during spring and from 54.80ng/ L at station VIII to 182.10ng/ L at station I during summer. Stations can be arranged as II < V < I < IV < III < VI < VII < VIII with values of 210.60, 185.70, 182.50, 181.30, 166.50, 149.90, 118.90, and 115.80ng/ L, during spring. During summer, stations I, V, II, VI, and III recorded values higher than those of stations IV, VII, and VIII, with values of 182.10, 147.50, 147.50, 124.60, 114.40, 103.50, and 54.80ng/ L. The results show that the stations with the highest concentrations are those located near the main drains (Bosaly, El-Khairiy, and Edku), which are all sources of sewage and agriculture and may be the main reason for the increase in iron concentrations in those areas (Villar *et al.*, 2006). On the other hand, low concentrations were detected near the Maadiya inlet, which is the confluence area between the Mediterranean Sea and the lake, which is considered a renewable and continuous area with water and is little influenced by human activities. During both seasons, BbF recorded total concentrations of 225.70ng/ L, with a minimum value of 20.80ng/ L at station VI and a maximum value of 34.50ng/ L at station II and an average of 28.21 ± 4.27 ng/ L during the spring; during the summer, BbF recorded 188.20ng/ L, with a minimum value of 15.90ng/ L at station III and a maximum value of 31.10ng/ L at station II with an average of 23.53 ± 5.01 ng/ L. Acy recorded the lowest concentration with a maximum value of 2.50ng/ L and an average of 1.43 ± 1.19 ng/ L during spring and a maximum value of 2.10ng/ L, with an average of 1.15 ± 0.97 ng/ L during summer. PAHs can enter water bodies through various pathways, including the deposition of airborne PAHs (Müller *et al.*, 2020), discharge of sewage water and runoff of stormwater (Patel *et al.*, 2020). Other significant sources include surface runoff from areas containing mines and coal storage places, liquid waste from industries related to wood processing, and various industrial activities related to these organic materials, such as dyes, medicines, pesticides, and

plastics (Ilyas *et al.*, 2019). Additionally, the release of liquid petroleum hydrocarbons due to oil spills and operations (petroleum pressing) is associated with the extraction of oil from raw materials (Castro *et al.*, 2022). Most PAHs are considered to be nonpolar and lipophilic and tend to dissolve in fats, oils, lipids, and water-insoluble, which makes their mobility in the aquatic environment limited (Gutman & Cyvin, 2012; Rand *et al.*, 2020). PAHs can be categorized according to Kanaly and Harayama (2000) and Jonathan *et al.* (2003), as low molecular weight PAHs composed of less than four aromatic rings (152- 178g/ mol) such as acenaphthene, acenaphthylene, anthracene, fluorene, and phenanthrene; medium molecular weight PAHs (202g/ mol)-fluoranthene and pyrene; and high molecular weight PAHs composed of four or more rings (228- 278g/ mol), such as benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, benzo[a]pyrene, benzo[e]pyrene, chrysene, dibenz[a,h]anthracene, and indeno[1,2,3-c,d]pyrene, as exhibited in Table (2). To determine the composition pattern of PAHs, the 16 PAHs studied could be divided into five groups: two-ring (2R), 3-ring (3R), 4-ring (4R), 5-ring (5R), and 6-ring. Table (2) and Figs (4, 5) display the concentrations of the 2-rings ranged from ND to 15.20, with an average of 8.50 ± 4.47 ng/ l during spring and from ND to 16.30, with an average of 9.26 ± 5.45 ng/ l during summer, which recorded the lowest percentage. The concentrations of the 3-rings fluctuated between 14.70 and 30.50 ng/ l, with an average of 23.11 ± 6.30 ng/ l during spring and from 12.00 to 37.10 ng/ l with an average of 19.58 ± 8.05 ng/ l during summer, and a percentage that ranged between 12 and 23% and from 11 to 17% during spring and summer, respectively. For the 4-rings, they are the most dominated rings in the lake, they ranged from 44.00 to 78.90, with an average of 62.76 ± 13.58 and from 25 to 60:63.10, with an average of 49.05 ± 12.41 ng/ l, and a percentage that ranged from 29 to 51% and from 33 to 44% during spring and summer, respectively. As for the 5-rings, they ranged from 24.00 to 46.90 with an average of 37.16 ± 8.25 and from 9.80 to 32.90 with an average of 20.80 ± 8.12 ng/ l with a percentage that ranged from 9 to 31% and from 19 to 28% during spring and summer, respectively. As for the 6-rings, they ranged from 14.40 to 54.70 ng/ l with an average of 32.36 ± 17.16 ng/ l and from ND to 46.90 ng/ l, with an average of 26.66 ± 18.28 ng/ l and a percentage that ranged from 15 to 36% and from 12 to 30% during spring and summer, respectively. Undetected values were observed at stations VII, and VIII during the summer.

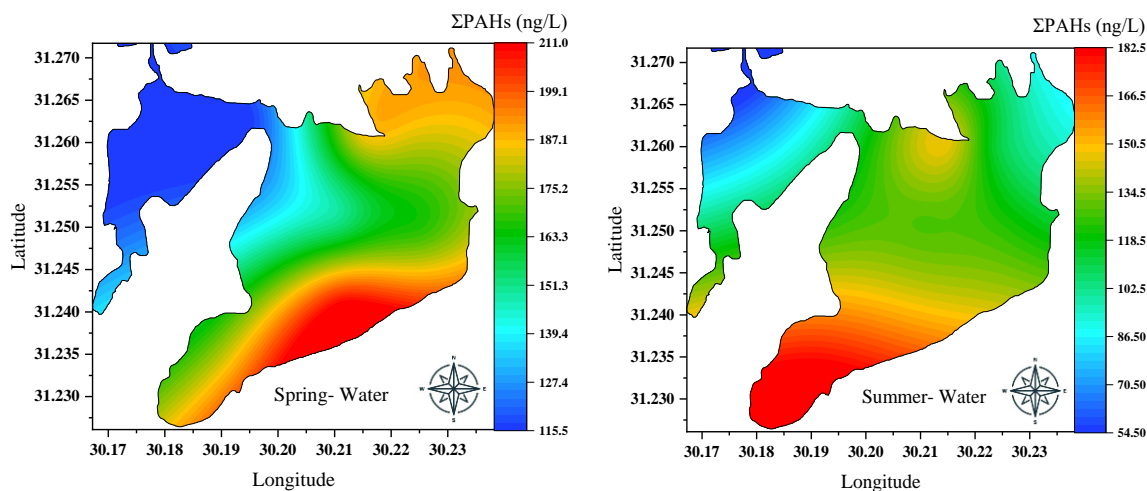


Fig. 2. Horizontal contours simulation of the distribution of total PAHs in Edku Wetland water during spring and summer 2022

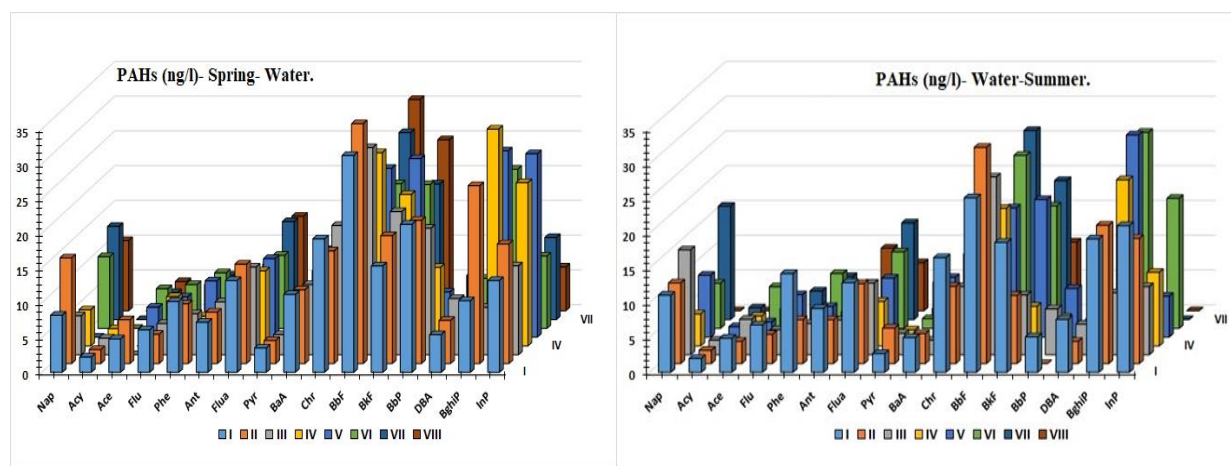


Fig. 3. Seasonal and regional values of total PAHs in Edku Wetland water during spring and summer 2022

Table 1. Seasonal and regional concentrations of PAHs in Edku Wetland water (ng/ l) during spring and summer 2022

PAH	I	II	III	IV	V	VI	VII	VIII	Min.	Max.	Aver.	SD
Nap	8.20	15.20	5.60	5.20	ND	10.30	13.40	10.10	ND	15.20	8.50	4.87
Acy	2.20	2.00	2.40	2.50	2.30	ND	ND	ND	ND	2.50	1.43	1.19
Ace	4.80	6.30	ND	ND	4.30	5.70	3.90	4.20	ND	6.30	3.65	2.39
Flu	6.10	4.20	4.50	7.10	5.80	6.30	ND	3.80	ND	7.10	4.73	2.23
Phe	10.20	8.60	5.90	4.30	8.10	8.00	6.40	0.00	ND	10.20	6.44	3.17
Ant	7.20	7.40	7.60	5.80	9.10	5.80	5.40	6.70	5.40	9.10	6.88	1.22
Flua	13.20	14.30	12.60	10.80	11.30	10.50	14.10	13.60	10.50	14.30	12.55	1.50

PAH	I	II	III	IV	V	VI	VII	VIII	Min.	Max.	Aver.	SD	
Pyr	3.50	3.30	2.90	ND	ND	ND	ND	ND	ND	3.50	1.21	1.68	
BaA	11.20	10.60	10.10	10.80	12.60	9.80	7.40	ND	ND	12.60	9.06	3.95	
Chr	19.20	16.20	18.60	14.30	14.00	11.50	ND	ND	ND	19.20	11.73	7.65	
BbF	31.20	34.50	29.80	27.80	24.30	20.80	26.90	30.40	20.80	34.50	28.21	4.27	
BkF	15.30	18.40	20.60	21.80	25.70	20.70	19.50	24.60	15.30	25.70	20.83	3.32	
BbP	21.30	20.60	18.20	11.30	6.50	ND	ND	5.10	ND	21.30	10.38	8.82	
DBA	5.40	6.20	8.10	4.90	8.50	7.20	4.50	2.90	2.90	8.50	5.96	1.91	
BghiP	10.30	25.60	6.80	31.20	26.80	22.90	5.60	8.10	5.60	31.20	17.16	10.45	
InP	13.20	17.20	12.80	23.50	26.40	10.40	11.80	6.30	6.30	26.40	15.20	6.78	
Σ	182.50	210.60	166.50	181.30	185.70	149.90	118.90	115.80	115.80	210.60	163.90	33.48	
Min.	2.20	2.00	ND	ND	ND	ND	ND	ND	ND	2.20	0.53	0.97	
Max.	31.20	34.50	29.80	31.20	26.80	22.90	26.90	30.40	22.90	34.50	29.21	3.56	
Aver.	11.41	13.16	10.41	11.33	11.61	9.37	7.43	-	7.43	13.16	10.67	1.84	
SD	7.56	8.88	7.97	9.81	9.36	7.10	7.87	-	7.10	9.81	8.36	1.00	
Summer	Nap	11.10	11.60	15.10	4.60	8.90	6.50	16.30	ND	ND	16.30	9.26	5.45
	Acy	2.00	1.90	2.10	ND	1.50	ND	1.70	ND	ND	2.10	1.15	0.97
	Ace	4.90	3.20	5.10	4.30	2.20	6.00	ND	1.30	ND	6.00	3.38	2.08
	Flu	6.80	4.20	3.60	5.40	6.10	ND	4.10	ND	ND	6.80	3.78	2.56
	Phe	14.20	6.30	4.50	ND	4.40	7.90	6.20	2.10	ND	14.20	5.70	4.25
	Ant	9.20	6.30	5.00	4.90	6.80	3.40	ND	9.00	ND	9.20	5.58	3.01
	Flua	12.90	11.50	10.30	6.40	8.50	11.00	13.90	6.90	6.40	13.90	10.18	2.71
	Pyr	2.70	5.10	3.10	2.30	ND	1.40	1.60	ND	ND	5.10	2.03	1.69
	BaA	5.00	4.30	2.10	9.20	8.60	ND	3.60	ND	ND	9.20	4.10	3.48
	Chr	16.50	11.10	9.80	13.20	14.00	ND	6.40	2.80	ND	16.50	9.23	5.73
	BbF	25.10	31.10	25.60	19.80	18.60	24.90	27.20	15.90	15.90	31.10	23.53	5.01
	BkF	18.70	9.80	8.60	5.70	19.80	17.60	20.00	9.90	5.70	20.00	13.76	5.82
	BbP	5.10	ND	6.60	4.10	7.00	ND	ND	6.90	ND	7.00	3.71	3.22
	DBA	7.60	3.20	4.40	ND	6.10	2.90	2.50	ND	ND	7.60	3.34	2.68
	BghiP	19.20	19.90	8.90	23.90	29.10	28.20	ND	ND	ND	29.10	16.15	11.77
	InP	21.10	18.00	9.80	10.60	5.90	18.70	ND	ND	ND	21.10	10.51	8.26
Σ	182.10	147.50	124.60	114.40	147.50	128.50	103.50	54.80	54.80	182.10	125.36	37.39	
Min.	2.00	ND	2.10	ND	ND	ND	ND	ND	ND	2.10	0.51	0.95	
Max.	25.10	31.10	25.60	23.90	29.10	28.20	27.20	15.90	15.90	31.10	25.76	4.61	
Aver.	11.38	9.22	7.79	7.15	9.22	8.03	6.47	-	6.47	11.38	8.47	1.63	
SD	7.12	8.08	5.94	6.86	7.65	9.40	8.37	-	5.94	9.40	7.63	1.12	

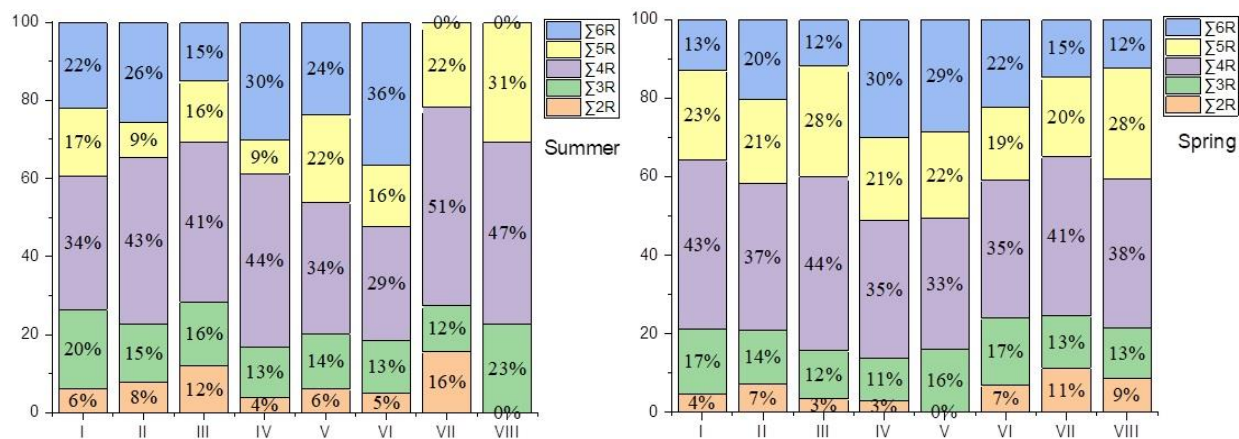


Fig. 4. Distribution and percentage of total PAHs rings of water samples during spring and summer in Edku Wetland water during 2022

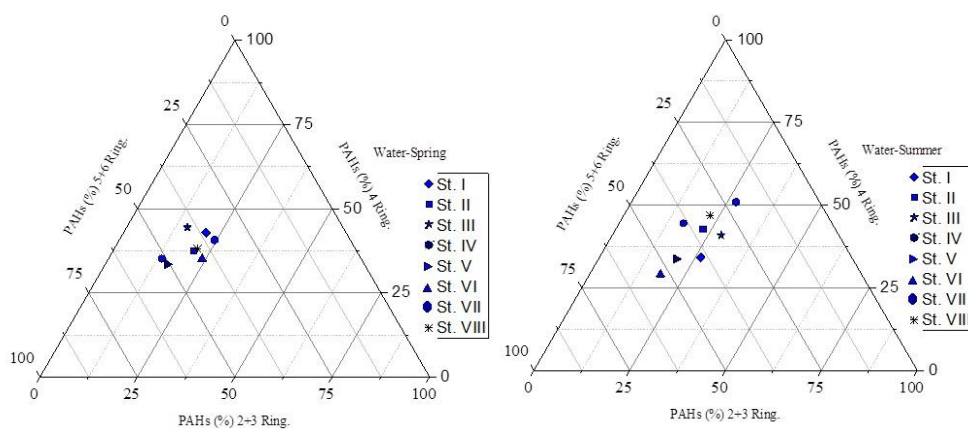


Fig. 5. PAHs ternary distribution plots (%) for Edku Wetland considering the congeners containing 2 + 3, 4, 5 + 6 cyclic rings

Refai *et al.* (2022) studied the occurrence and distribution of polycyclic aromatic hydrocarbons (PAHs) in the water surface of the Nile in Egypt in three locations downstream; the study spotted an increase in the concentration of polycyclic aromatic hydrocarbons near the Alexandria region. Moreover, these concentrations are higher compared to some rivers in Europe, as well as higher than the levels specified for drinking water in the United States of America.

1. The sources of PAHs in surface water

The ratios $\Sigma\text{LMW}/\Sigma\text{HMW}$, $\text{AN}/(\text{AN} + \text{Phen})$, $\text{Flur}/(\text{Flur} + \text{Pye})$, $\text{BaA}/(\text{BaA} + \text{Chry})$, and $\text{In}/(\text{In} + \text{BgP})$ were used to determine the source and origin of polycyclic aromatic hydrocarbons in water; the ratio $\Sigma\text{LMW}/\Sigma\text{HMW}$ lower than 1 refers to a dominant pyrolytic input rather than petrogenic (**Hasanati *et al.*, 2011; Kafilzadeh *et al.*, 2011**). $\text{AN}/(\text{AN} + \text{Phen})$

<0.1 refers to petroleum and petrogenic sources; >0.1 refers to combustion sources; Flur/ (Flur + Pye) resulting between 0.4 and 0.5 refers to fuel combustion, while a ratio more than 0.5 refers to coal, grass, and wood burning (**Zhu *et al.*, 2008**). On the other hand, BaA/ (BaA + Chry) more than 0.35 refers to coal, grass, and wood burning, and less than 0.2 refers to a petrogenic source (**Wang *et al.*, 2007**); In/ (In + BgP) more than 0.5 indicates coal, grass, and wood burning sources, and the range between 0.2 and 0.5 refers to fuel combustion sources (**Tobiszewski, 2014**). LMW/ HMW greater than 1 refers to petrogenic source; less than 1 refers to a pyrogenic source (**Suman *et al.*, 2016**).

In the current study, Ant/ Ant+Phe ratios ranged between 0.41 and 1.00- NA and 1.00 during spring and summer, respectively, indicating that the PAHs present at all stations were derived from petrogenic and petroleum sources. Flur/ Flur + Pye ratios ranged between 0.56: 1.00- NA: 1.00 during spring and summer, respectively, indicating that the PAHs pollutant at all stations was derived from pyrolytic sources (coal, grass, and wood burning) during spring and summer. Stations VI and VIII during the summer recorded a petrogenic source. BaA/ BaA + Chry ratios recorded a maximum value of 1.00 and 0.41 during spring and summer, respectively. All stations recorded coal, grass, and wood burning pollution sources, except stations VIII during spring and summer and stations III and VI during summer, which recorded petrogenic sources. In/ In + BgP ratios ranged from 0.31 to 0.68 during the spring and reached 0.52 during the summer. All stations during spring and summer recorded a petrogenic pollution (fuel combustion), except stations I, III, and VII during spring, while stations I and III during summer recorded coal, grass, and wood burning as PAHs water pollution sources. Σ LMW/ Σ HMW recorded values that ranged from 0.16: 0.32 - 0.20: 0.40 during spring and summer, respectively, referring to pyrogenic sources, as shown in Table (2).

Ahmed *et al.* (2017) measured organic sources for polycyclic aromatic hydrocarbons (PAHs) in seawater samples that were collected from different regions around the Alexandria coastal area. The results of the research showed that the concentrations of organic substances ranged between 8.97 and 1254.76ng/ l, and these concentrations exceeded the permissible limits, according to the water standard in the European Union, and that the source of these compounds is the pyrogenic sources resulting from the incomplete combustion of fuel used in ships, boats, and vehicle engines. Compared to the petrogenic sources, the high concentration of these compounds may pose health risks to aquatic organisms. **Refai *et al.* (2022)** studied the spatial distribution of polycyclic aromatic hydrocarbons in surface water samples on the Egyptian Mediterranean coast (Alexandria to Manzallah) and referred to the distribution of PAHs value increasing from west to east, which was controlled by water circulation in the Mediterranean Sea, and the levels of PAHs in near-shore locations were lower than those of middle and onshore locations. They also referred to the fact that the reason for the increase in concentrations is due to wind-induced waves re-suspend rich PAHs from sediment, and the diagnostic ratios indicated pyrogenic origin. **El-Naggar *et al.* (2018)** addressed the detection of polycyclic aromatic hydrocarbons in water along Alexandria's coastal water in Egypt during winter 2015 by using gas chromatographic techniques to determine the sources of PAH pollution in water. They also noticed that the PAH

concentrations were higher than the permissible limits of the European Union standards for water quality and that the high molecular weight (HMW) of PAHs included 4, 5, and 6 rings. They postulated that the sources of PAHs in the studied area were mostly of a pyrolytic origin, derived from and resulting from the incomplete combustion of fuel in ships, boats, and cars.

2. Toxicity and ecological risk assessment

The ecological risks of PAHs in lake water were determined by using risk quotients (RQ) through comparing the exposure concentration and toxicity reference values.

$$RQ = C_{PAHs} / C_{QV}$$

Where, RQ: Risk quotients; C_{PAHs} is the concentration \sum PAHs in water samples, and C_{QV} is the quality value of PAHs. If the $RQ > 1$ refers to potential ecological hazards. To obtain more accurate data, minimum (NCs) and maximum (MPCs) concentrations are used,

$$RQ = C_{PAHs} / C_{QV} (NCs) \quad \text{and} \quad RQ = C_{PAHs} / C_{QV} (MPCs)$$

Where, RQ_{NCs} less than 1 refers to negligible pollution that could be ignored, and more than 1 refers to moderate pollution; RQ_{MPC} less than 1 refers to moderate pollution, and more than 1 refers to severe pollution (**Petry *et al.*, 1996; Cao *et al.*, 2010**).

During the present study, the risk quotient levels of \sum 16 PAHs in the water environment from Edku Wetland during spring and summer recorded values below 1.00. Comparing the results with risk quotients ranks the results recorded as ignored PAH pollution, and it does not represent any observed hazard to the environment, as illustrated in Table (3).

BaP toxic equivalent agents were used to assess the health and environmental risks resulting from polycyclic aromatic hydrocarbon pollution by determining the ratio between water concentrations of B(a)P equivalents and the concentrations of B(a)P alone according to **Petry *et al.*, (1996)**; the B(a)P was selected which it is considered to be the highest carcinogenic PAHs (**Pufulete *et al.*, 2004**). According to the results, the maximum BaP equivalent from the eight samples collected from the different locations in the lake was recorded at 24.60 μ g/ kg during the spring and 12.58 μ g/ kg during the summer, as illustrated in Table (3).

Table 2. Seasonal and regional levels for different rings and sources of PAHs in surface water from Edku Wetland during spring and summer 2022

	St.'s	Σ 16PAHs	Σ 2R	Σ 3R	Σ 4R	Σ 5R	Σ 6R	Σ LMW	Σ HMW	L/H	An/ An+Phe	Flur/ Flur + Pye	BaA/ BaA + Chry	In/ In + BgP
Spring	I	182.50	8.20	30.50	78.30	42.00	23.50	38.70	143.80	0.27	0.41	0.64	0.37	0.56
	II	210.60	15.20	28.50	78.90	45.20	42.80	43.70	166.90	0.26	0.46	0.56	0.40	0.40
	III	166.50	5.60	20.40	74.00	46.90	19.60	26.00	140.50	0.19	0.56	0.61	0.35	0.65
	IV	181.30	5.20	19.70	63.70	38.00	54.70	24.90	156.40	0.16	0.57	1.00	0.43	0.43
	V	185.70	0.00	29.60	62.20	40.70	53.20	29.60	156.10	0.19	0.53	1.00	0.47	0.50
	VI	149.90	10.30	25.80	52.60	27.90	33.30	36.10	113.80	0.32	0.42	1.00	0.46	0.31
	VII	118.90	13.40	15.70	48.40	24.00	17.40	29.10	89.80	0.32	0.46	1.00	1.00	0.68
	VIII	115.80	10.10	14.70	44.00	32.60	14.40	24.80	91.00	0.27	1.00	1.00	0.00	0.44
	Min.	115.80	0.00	14.70	44.00	24.00	14.40	24.80	89.80	0.16	0.41	0.56	0.00	0.31
	Max.	210.60	15.20	30.50	78.90	46.90	54.70	43.70	166.90	0.32	1.00	1.00	1.00	0.68
	Ave.	163.90	8.50	23.11	62.76	37.16	32.36	31.61	132.29	0.25	0.55	0.85	0.43	0.50
	SD.	33.48	4.87	6.30	13.58	8.25	16.17	7.07	30.23	0.06	0.19	0.21	0.27	0.13
Summer	I	182.10	11.10	37.10	62.20	31.40	40.30	48.20	133.90	0.36	0.39	0.72	0.23	0.52
	II	147.50	11.60	21.90	63.10	13.00	37.90	33.50	114.00	0.29	0.50	0.45	0.28	0.47
	III	124.60	15.10	20.30	50.90	19.60	18.70	35.40	89.20	0.40	0.53	0.54	0.18	0.52
	IV	114.40	4.60	14.60	50.90	9.80	34.50	19.20	95.20	0.20	1.00	0.70	0.41	0.31
	V	147.50	8.90	21.00	49.70	32.90	35.00	29.90	117.60	0.25	0.61	1.00	0.38	0.17
	VI	128.50	6.50	17.30	37.30	20.50	46.90	23.80	104.70	0.23	0.30	0.00	0.00	0.40
	VII	103.50	16.30	12.00	52.70	22.50	0.00	28.30	75.20	0.38	0.00	0.72	0.36	0.00
	VIII	54.80	0.00	12.40	25.60	16.80	0.00	12.40	42.40	0.29	0.81	0.00	0.00	0.00
	Min.	54.80	0.00	12.00	25.60	9.80	0.00	12.40	42.40	0.20	0.00	0.00	0.00	0.00
	Max.	182.10	16.30	37.10	63.10	32.90	46.90	48.20	133.90	0.40	1.00	1.00	0.41	0.52
	Ave.	125.36	9.26	19.58	49.05	20.81	26.66	28.84	96.53	0.30	0.52	0.52	0.23	0.30
	SD.	37.39	5.45	8.05	12.41	8.12	18.28	10.89	28.42	0.07	0.31	0.36	0.16	0.22

Notably, the maximum BaP equivalent for studied samples is lower than the cancer CV for benzo(a)pyrene (65µg/ kg, or 0.065ppm), according to **Atsdr (2022)**. Moreover, method B cleanup level for benzo(a)pyrene was 0.137mg/ kg, according to **Washington State Department of Ecology (2007)**. It indicates the safety of the lake water from the possibility of cancer. These possibilities coincide with those of **Haiba (2019)**, who elucidated that the source of PAHs in the River Nile surface water was pyrogenic (Coal, grass, and wood burning and fuel combustion).

Table 3. Toxic equivalence quantities (BaP-TEQs) and mean values of RQ(NCs) and RQ(MPCs) of PAHs in Edku Wetland water during 2022

Compound	Abb.	AR	MW	TEFs	NCs	MPCs	BaP (Spring)	BaP (Summer)	RQ(NCs) (Spring)	RQ(NCs) (Summer)
Naphthalene	Nap	2	128	0.001	12000	1200000	0.01	0.01	0.00	0.00
Acenaphthylene	Acy	3	152	0.001	700	70000	0.00	0.00	0.00	0.00
Acenaphthene	Ace	3	154	0.001	700	70000	0.00	0.00	0.01	0.00
Fluorene	Flu	3	166	0.001	700	70000	0.00	0.00	0.01	0.00
Phenanthrene	Phe	3	178	0.001	3000	300000	0.01	0.01	0.00	0.00
Anthracene	Ant	3	178	0.01	700	70000	0.07	0.06	0.01	0.00
Fluoranthene	Flua	4	202	0.001	3000	300000	0.01	0.01	0.00	0.00
Pyrene	Pyr	4	202	0.001	700	70000	0.00	0.00	0.00	0.00
Benzo(a)anthracene	BaA	4	228	0.1	100	10000	0.91	0.41	0.09	0.00
Chrysene	Chr	4	228	0.01	3400	340000	0.12	0.09	0.00	0.00
Benzo(b)Fluoranthene	BbF	4	252	0.1	100	10000	2.82	2.35	0.28	0.00
Benzo(k)Fluoranthene	BkF	5	252	0.1	400	40000	2.08	1.38	0.05	0.00
Benzo(a) Pyrene	BbP	5	252	1	500	50000	10.38	3.71	0.02	0.00
Dibenz(a,h)anthracene	DBA	5	278	1	500	50000	5.96	3.34	0.01	0.00
Benzo(g,h,i) perylene	BghiP	6	252	0.01	300	30000	0.17	0.16	0.06	0.00
Indeno(1,2,cd)pyrene	InP	6	276	0.1	400	40000	1.52	1.05	0.04	0.00
TEQΣPAHs							24.06	12.58		

3. Incremental lifetime cancer risk (ILCR) for PAHs in water

Given the potential risks associated with polycyclic aromatic hydrocarbon pollution of water due to ingestion, absorption, or inhalation, it was necessary to assess the incremental lifetime cancer risk (ILCR) for water environment under study. This assessment determines the likelihood that exposure to these substances will result in cancer. The total carcinogenic risk was calculated according to the following equations and is illustrated in Table (4).

$$\text{Cancer risk}_{\text{ingest}} = \frac{C_{\text{water}} \times \text{IngR} \times \text{EF} \times \text{ED} \times \text{CF} \times \text{SFO}}{\text{BW} \times \text{AT}}$$

$$\text{Cancer risk}_{\text{derma}} = \frac{C_{\text{water}} \times SA \times AF_{\text{sediment}} \times ABS \times EF \times ED \times CF \times SFO \times GIABS}{BW \times AT}$$

$$\text{Cancer risk}_{\text{inhale}} = \frac{C_{\text{water}} \times EF \times ED \times ET \times IUR}{PET \times AT^*}$$

$$\text{Total ILCR} = \sum \text{Cancer risk}_{\text{ingest}} + \text{Cancer risk}_{\text{derma}} + \text{Cancer risk}_{\text{inhale}}$$

Where, *C* represents the concentration in the sediment samples (µg/ k); *CF* is the conversion coefficient: 1 × 10⁻⁶kg/ mg; *SA* is exposed skin area of dermal contact with water: 5700cm² for adult and 2800cm² for child; *AF* is skin adherence factor (mg/ cm²): 0.2 for adult and 0.07 for child:0.4; *ABS* is adsorption coefficient of dermal: 0.13 for adult and child (Huang *et al.*, 2014); *AT* is average life span (Day): 18980 for adult and child (Papadakis *et al.*, 2015); *EF* is exposure frequency (day/ year): 313 for adult and child; *ED* is exposure duration (year): 24 for adult and 8 for child (Qu *et al.*, 2015; Tongo *et al.*, 2017), and *BW* is adult body weight (kg): 60 for adult and 15 for child (Tongo *et al.*, 2017). *IngR* is ingestion rate (mg/ day): 200 for adult and 100 for child (Tongo *et al.*, 2017); *ET* is exposure time (h/ day): 8 for adult and child; *SFO* is oral slope factor (mg/ kg/ day)⁻¹: 7.3 for adult and child; *GIABS* is gastrointestinal absorption factor (mg/ kg/ day)⁻¹: 1 for adult and child; *IUR* is inhalation unit risk (mg/ m3)⁻¹: 1.1 × 10⁻⁶ for adult and child; *AT* is average time (h): 455520 for adult and child; *PEF* is particle emission factor (mg/kg): 1.36 × 10⁹ for adult and child (Qu *et al.*, 2015; Tongo *et al.*, 2017).

The incremental lifetime cancer risk (ILCR) guideline is ranked as ≤ 10⁻⁶ Very low, 10⁻⁶:10⁻⁴ low, 10⁻⁴: 10⁻³ Moderate, 10⁻³, :10⁻¹ High, ≥10⁻¹ Very high. Very low refers to no risk or negligible risks; low, moderate, high, or very high refer to high risk, which may cause harmful health effects and cancer.

In the present study, as shown in Table (4), the cancer risks for ingestion exposure in adults ranged from 1.06 × 10⁻⁶:1.82 × 10⁻⁶, with an average of 1.37 × 10⁻⁶ during the spring and from 6.80 × 10⁻⁷:1.73 × 10⁻⁶, with an average of 1.36 × 10⁻⁶ during the summer. Cancer risks for dermal exposure for adults ranged from 7.25 × 10⁻⁸:1.24 × 10⁻⁷, with an average of 9.34 × 10⁻⁸ during the spring and from 9.69 × 10⁻⁸:1.18 × 10⁻⁷, with an average of 9.30 × 10⁻⁸ during the summer. Cancer risks for inhalation exposure for adults ranged from 2.05 × 10⁻¹⁷:3.52 × 10⁻¹⁷, with an average 2.65 × 10⁻¹⁷ during spring and from 1.31 × 10⁻¹⁷:3.35 × 10⁻¹⁷, with an average 2.64 × 10⁻¹⁷ during summer. On the other hand, child cancer risks for ingestion exposure ranged from 2.04 × 10⁻⁶:3.50 × 10⁻⁶, with an average 2.63 × 10⁻⁶ during spring and from 1.30 × 10⁻⁶:3.33 × 10⁻⁶, with an average 2.62 × 10⁻⁶ during summer. Cancer risks for dermal exposure ranged from 6.97 × 10⁻⁷:1.18 × 10⁻⁵, with an average 7.88 × 10⁻⁶ during spring and from 5.30 × 10⁻⁷:1.35 × 10⁻⁶, with an average 1.66 × 10⁻⁶ during summer. Cancer risks for inhalation exposure for adults ranged from 5.14 × 10⁻¹⁸:8.81 × 10⁻¹⁸, with an average 6.62 × 10⁻¹⁸ during spring and from 3.29 × 10⁻¹⁸:8.38 × 10⁻¹⁸, with an average 8.52 × 10⁻¹⁸ during summer.

Incremental lifetime cancer risk during spring ranged from 1.13×10^{-6} : 1.95×10^{-6} with an average of 1.014×10^{-6} for adults, and from 4.19×10^{-6} : 1.52×10^{-5} with an average of 1.50×10^{-5} for children; during summer, it fluctuated between 7.26×10^{-7} : 1.85×10^{-6} with an average of 1.46×10^{-6} for adults, and 1.85×10^{-6} : 4.68×10^{-6} with an average of 3.68×10^{-6} . Upon comparing the results with the New York State Department of Health regulatory guidelines, it is evident that the incremental lifetime cancer risk is very low. **Refai *et al.* (2022)** assessed the PAH levels in terms of exposure and cancer risk assessment in the Nile by determining 16 PAHs in 50 water samples, and they deduced a chance for cancer risk by determining the incremental lifetime cancer risk.

4. Statistical analysis

The Originlab 2019 programme was used for the determination of factor analysis, principal component analysis (PCA), and cluster analysis, as is the case in most environmental studies for the determination of correlations and multivariate statistical methods.

Table 4. Incremental lifetime cancer risk (ILCR) for PAHs in water for Edku Wetland during spring and summer 2022

Exposure	Season		I	II	III	IV	V	VI	VII	VIII	Min.	Max.	Aver.
Ingestion	Spring	Adult	9.15E-07	1.06E-06	8.35E-07	9.09E-07	9.31E-07	7.52E-07	5.96E-07	5.81E-07	5.81E-07	1.06E-06	8.22E-07
Ingestion	Spring	Child	1.76E-06	2.03E-06	1.60E-06	1.75E-06	1.79E-06	1.44E-06	1.15E-06	1.12E-06	1.12E-06	2.03E-06	1.58E-06
Ingestion	Summer	Adult	9.13E-07	7.40E-07	6.25E-07	5.74E-07	7.40E-07	6.45E-07	5.19E-07	2.75E-07	2.75E-07	9.13E-07	6.29E-07
Ingestion	Summer	Child	1.75E-06	1.42E-06	1.20E-06	1.10E-06	1.42E-06	1.24E-06	9.97E-07	5.28E-07	5.28E-07	1.75E-06	1.21E-06
Dermal	Spring	Adult	6.24E-08	7.21E-08	5.70E-08	6.20E-08	6.35E-08	5.13E-08	4.07E-08	3.96E-08	3.96E-08	7.21E-08	5.61E-08
Dermal	Spring	Child	3.51E-07	7.21E-06	5.70E-06	6.20E-06	6.35E-06	5.13E-06	4.07E-06	3.96E-06	3.51E-07	7.21E-06	4.87E-06
Dermal	Summer	Adult	6.23E-08	5.05E-08	4.26E-08	3.91E-08	5.05E-08	4.40E-08	3.54E-08	1.88E-08	1.88E-08	6.23E-08	4.29E-08
Dermal	Summer	Child	7.12E-07	5.77E-07	4.87E-07	4.47E-07	5.77E-07	5.02E-07	4.05E-07	2.14E-07	2.14E-07	7.12E-07	4.90E-07
Inhalation	Spring	Adult	1.77E-17	2.04E-17	1.62E-17	1.76E-17	1.80E-17	1.45E-17	1.15E-17	1.12E-17	1.12E-17	2.04E-17	1.59E-17
Inhalation	Spring	Child	4.43E-18	5.11E-18	4.04E-18	4.40E-18	4.50E-18	3.64E-18	2.88E-18	2.81E-18	2.81E-18	5.11E-18	3.97E-18
Inhalation	Summer	Adult	1.77E-17	1.43E-17	1.21E-17	1.11E-17	1.43E-17	1.25E-17	1.00E-17	5.32E-18	5.32E-18	1.77E-17	1.22E-17
Inhalation	Summer	Child	4.42E-18	3.58E-18	3.02E-18	2.77E-18	3.58E-18	3.12E-18	2.51E-18	1.33E-18	1.33E-18	4.42E-18	3.04E-18
Total ILCR	Spring	Adult	9.78E-07	1.13E-06	8.92E-07	9.71E-07	9.95E-07	8.03E-07	6.37E-07	6.20E-07	6.20E-07	1.13E-06	8.78E-07
	Spring	Child	2.11E-06	9.23E-06	7.30E-06	7.95E-06	8.14E-06	6.57E-06	5.21E-06	5.08E-06	2.11E-06	9.23E-06	6.45E-06
	Summer	Adult	9.76E-07	7.90E-07	6.68E-07	6.13E-07	7.90E-07	6.89E-07	5.55E-07	2.94E-07	2.94E-07	9.76E-07	6.72E-07
	Summer	Child	2.47E-06	2.00E-06	1.69E-06	1.55E-06	2.00E-06	1.74E-06	1.40E-06	7.42E-07	7.42E-07	2.47E-06	1.70E-06

Principal component analysis (PCA)

The statistical analysis indicated that there are two main factors with a direct impact, and they can be explained as follows: The first factor represented 38.89% during spring and 35.94% during summer of the total variance, as illustrated in Fig. (6). During spring, all stations recorded a strong positive loading, reaching 0.37, except Nap, Ace, Flua, and BKF, which recorded a negative loading. During summer, it reached 0.34 except for Flu, InP, BKF, DBA, and BghiP, which recorded a negative loading. The first component may be suggested due to anthropogenic activities, such as domestic activities and discharging wastewater. The second factor that can be suggested is that these compounds could be transferred to the lake from the drains that lead to their accumulation and deposit in the lake. The second factor recorded 26.56 and 22.12% during spring and summer, respectively, of total variance, which owned a positive loading with Nap (0.28), Acy (0.10), Ace (0.11), Phe (0.16), Ant (0.03), Flua (0.38), Pyr (0.43), BaA (0.01), Chr (0.13), BbF (0.40), and BaP (0.35) during spring; Acy (0.03), Ace (0.13), Flu (0.34), Ant (0.35), BaA (0.39), Chr (0.41), BaP (0.37), DBA (0.18), BghiP (0.27), and InP (0.10) during summer, as illustrated in Fig. (6).

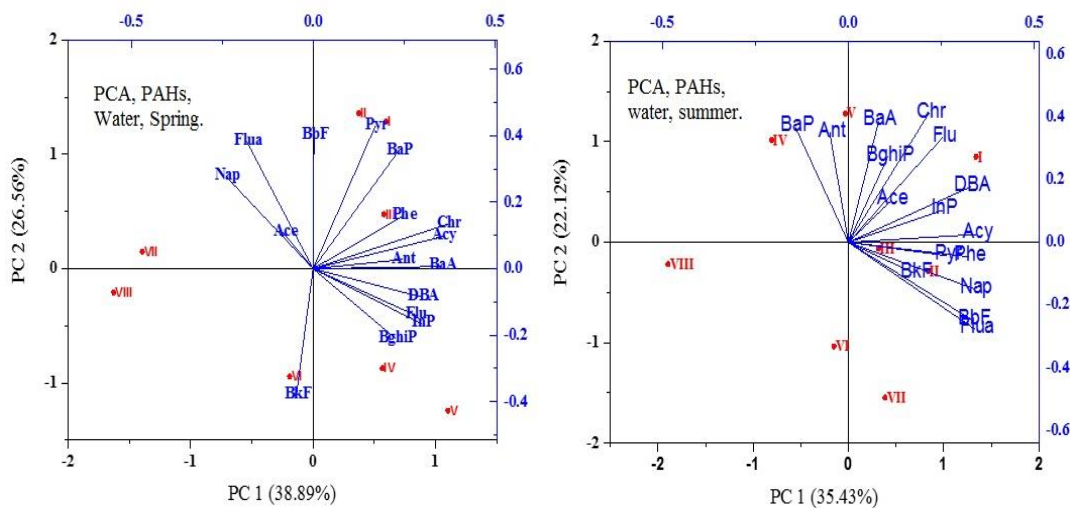


Fig. 6. Loading matrix of the first two principal components of PAHs in Edku Wetland water during spring and summer 2022

Hierarchical cluster analysis (HCA)

Single linkages

Hierarchical cluster analysis (HCA) was used to determine similarities or distance among sampling locations based on the concentration of PAHs in water samples during spring and summer. The results in Fig. (7) revealed three principal clusters during spring, two during summer, and seven stages for each season. The first stage contains stations I and III at a distance of 10.62; the second stage contains stations IV and V at a distance of 12.94; the third stage contains stations VII and VIII at a distance of 15.05; the fourth

stage contains stations I and II at a distance of 18.43; the fifth stage contains stations I and IV at a distance of 20.29; the sixth stage contains stations I and VI at a distance of 22.17, and the seventh stage contains stations I and VII at a distance of 23.52 during spring. During summer, the first stage contains stations I and II at a distance of 16.99; the second stage contains stations I and III at a distance of 17.27; the third stage contains stations IV and V at a distance of 18.82; the fourth stage contains stations I and VI at a distance of 19.76; the fifth stage contains stations I and VI at a distance of 20.04; the sixth stage contains stations I and VII at a distance of 20.97, and the seventh stage contains stations I and VIII at a distance of 25.42. During spring, three distinct groups emerged: the first group was formed from stations VII and VIII with a high distance of 16 units and the lowest concentration; the second group contained stations IV and V with a distance of 13 units and the highest concentration; and the third group contained stations I and III with a distance of 10 units and intermediate concentration. During the summer, the results showed remarkable similarity between the different stations.

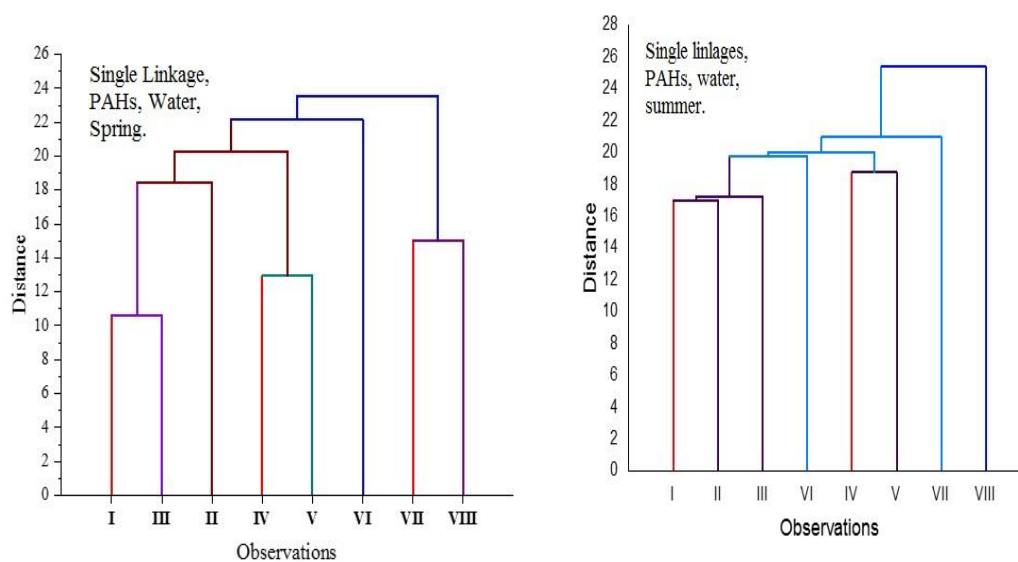


Fig. 7. Hierarchical cluster analysis dendrogram (single linkage) showing the spatial distribution of PAHs among different sampling sites in Edku Wetland water during the spring and summer 2022

Complete linkage

Data illustrated in Fig. (8) show that, stage (1) exhibited a linkage between Acy and Pyr with a distance of 3.89; stage (2) was between Ant and DBA with a distance of 4.83; stage (3) was between Phe and Ant with a distance of 7.52; stage (4) was between Flu and Phe with a distance of 8.70; stage (5) was between Acy and Ace with a distance of 10.24; stage (6) was between Flu and BaA with a distance of 12.01; stage (7) was

between Acy and Flu with a distance of 15.10; stage (8) was between Nap and Flua with a distance of 15.70; stage (9) was between Chr and BaP with a distance of 15.73; stage (10) was between BghiP and InP with a distance of 19.30; stage (11) was between Nap and Acy with a distance of 21.43; stage (12) was between BkF and BghiP with a distance of 26.32; stage (13) was between Nap and Chr with a distance of 26.69; stage (14) was between BbF and BkF with a distance of 38.28, and stage (15) was between Nap and BbF with a distance of 44.46 during spring. Whereas during summer, stage (1) showed a linkage between Acy and Pyr with a distance of 4.61; stage (2) was between Flu and BaA with a distance of 5.14; stage (3) was between Acy and Ace with a distance of 7.68; stage (4) was between Ant and BaP with a distance of 8.16; stage (5) was between Acy and Flu with a distance of 8.70; stage (6) was between Nap and Flua with a distance of 9.88; stage (7) was between Acy and Ant with a distance of 10.16; stage (8) was between Acy and Phe with a distance of 11.60; stage (9) was between Nap and Chr with a distance of 14.09; stage (10) was between Nap and BkF with a distance of 17.17; stage (11) was between Nap and InP with a distance of 20.94; stage (12) was between Nap and Acy with a distance of 24.32; stage (13) was between Nap and Chr with a distance of 25.20; stage (14) was between BbF and BghiP with a distance of 39.62, while stage (15) was between Nap and BbF with a distance of 47.15 (Ogbuagu *et al.*, 2011). On the other hand, anthropogenic sources may be the main source that has an effect on concentration (Moses *et al.*, 2015).

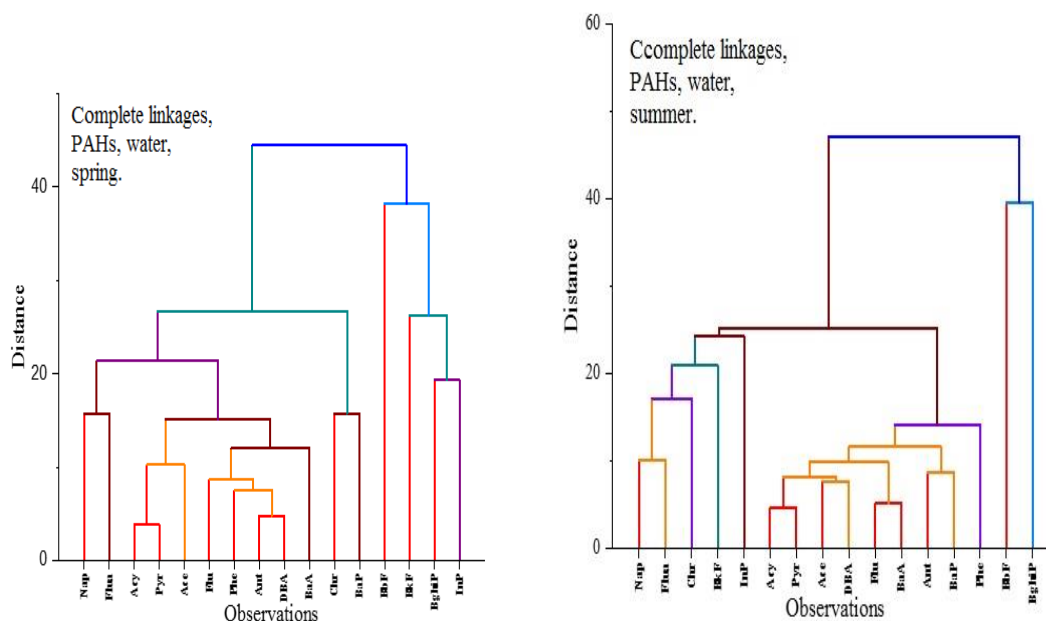


Fig. 8. Hierarchical cluster analysis dendrogram (complete linkage) between group for PAHs in water samples from Edku Wetland during the spring and summer 2022

CONCLUSION

The concentrations of 16 PAH compounds ranged from ND to 34.5 µg/L, all falling below the permissible limits and posing no effect on aquatic organisms. The study's findings are consistent with those of similar studies conducted internally and are lower than some recorded externally. Urbanized areas and points of convergence of drains with the lake showed a high level of PAH contamination, contrary to the Bogaz area (the linked point of the sea with the lake), which recorded the lowest values and the lowest rate of pollution. The results of PAH molecular ratios indicated a variety of PAH sources that ranged between petrogenic and pyrolytic sources. The evaluation of ecotoxicological indicated a low level of risk.

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