

## Occurrence and Distribution of Polycyclic Aromatic Hydrocarbons in Aquatic Environment of Ismailia Canal, Egypt

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**Abstract:** Persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs) are of great concern due to their persistence, bioaccumulation and toxic effects. In this study, water samples were collected in four seasons during 2011–2012 from nine catchment areas that represent the aquatic environment of Ismailia canal in Egypt. The distribution of 16 PAHs included in the US Environmental Protection Agency's (EPA) priority pollutant list was analyzed by gas chromatography/flame ionization detector (GC/FID). Total PAH concentrations ranged from 1822 to 13170 ng/L in summer samples, for autumn the concentrations were in the range 866 to 5217 ng/L, for spring the concentrations were in the range 697 to 5960 ng/L, and for winter concentrations ranged from 926 to 5217 ng/L. The PAH profiles were dominated by low molecular weight PAHs (two- and three-ring components) in all collected water samples. The origin of PAHs in all water samples in this study areas may be from oil or other industrial contamination.

[Hossam S. Jahin, Al-Shimaa E. Nassar, Mohammed M. Yehya and Ashraf F. Wasfi. **Occurrence and Distribution of Polycyclic Aromatic Hydrocarbons in Aquatic Environment of Ismailia Canal, Egypt.** *J Am Sci* 2015;11(4):176-182]. (ISSN: 1545-1003). <http://www.jofamericanscience.org>. 20

**Keywords:** Polycyclic Aromatic Hydrocarbons (PAHs), GC/FID, Ismailia canal, Egypt. .

### 1. Introduction

Water pollution by toxic organic compounds is a topic of worldwide concern contamination such as Polycyclic Aromatic Hydrocarbons (PAHs) which are ubiquitous in the environment and known for their carcinogenic and mutagenic properties and for being responsible of background level contamination in environmental matrices. Polycyclic Aromatic Hydrocarbons (PAHs) have two or more fused benzoid rings and no elements other than carbon and hydrogen [1].

Polycyclic Aromatic Hydrocarbons (PAHs) are included in the priority lists of pollutants of the U.S. Environmental protection Agency (EPA) and the European union. The U.S. EPA fixed 16 parent PAHs as priority pollutants, the latest being effective from 1997,[2\_6]. Some of which are considered to be possible or probable to human carcinogens. The endocrine disrupting properties of PAHs have been reported[7,8]. The distribution in the environment and potential human health risks have thus become the focus of much attention.

PAHs are formed from natural and anthropogenic sources. Natural PAHs are mainly from volcanic eruptions, plant emissions and natural fires. Anthropogenic PAHs are mostly generated during the combustion of carbonaceous materials such as coals, gasoline, and diesel [9].

According to the formation mechanism, anthropogenic PAHs can be classified to pyrolytic and petrogenic, pyrolytic PAHs are formed as consequence

of incomplete fuel combustion whereas petrogenic PAHs are mainly derived from the crude oil or unburned fuel and its refined products [10].

In this study an extensive and systematic survey has been undertaken to evaluate the spatial variation, contamination status, and sources of PAHs in Ismailia canal which, is one of the fresh water sources in the east sector of Egypt.

### 2. Material and Methods

#### *Chemicals and reagents.*

Sixteen PAHs of primary environmental concern according to the EPA, were analysed in this study: naphthalene, acenaphthene, flurene, phenanthrene, anthracene, flouranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)flouranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene and benzo(ghi)perylene. The PAHs were purchased from supelco (belle fonte, PA, USA) as a mixed solution of 2000 µg/ml each in Hexane:benzene (50:50). The internal standard was a mixture containing naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, 1,4-dichlorobenzene-d4 and perylene-d12 supplied by Supelco as a mixed solution of 2000 µg/ml in Hexane. The surrogate spike was 500 µg/ml mixture in Hexane containing 2-flurobiphenyle and 4-terphenyle-d14 supplied by Supelco. Working standards of PAHs were prepared by combining the standard mixture with the corresponding internal standard stock solution, respectively. These solutions were further diluted with solvent to prepare calibration solutions in the range 0.05\_2 µg/ml.

All solvents used for sample processing and analysis (dichloromethane, acetone, hexane and toluene) were HPLC grade. De-ionized water taken from a Milli-Q system (Millipore, Watford, uk).

#### Area description and Sampling Locations

Ismailia Canal was constructed in 1862 by virtue of two agreements between the Egyptian government and the Suez Canal Company, for creating a navigable waterway between the Nile and the Suez Canal. Today its water is only used for irrigation and to provide drinking water for towns along its course. The canal has its inlet from the Nile at Cairo and runs directly to the east to the town of Ismailia passing the governorates of Cairo – Kalioubeya – Sharkeya and Ismailia (Fig.1).

Along the canal there are several sources of pollution – industries in the region of Cairo as well as

agricultural run-offs in the eastern part. For example the El-Mahsama pumping station was built to pump drainage water from the El-Mahsama Drain into the Ismailia canal. Because of pressure from the local governments, the mixing station was closed in 1994 [11].

The samples from Ismailia Canal taken in four seasons (locations from 1 to 9) total 36 samples were collected during summer (on 26 August 2011- from 12.00 p.m. to 4.00 p.m.- air temperature was 33°C), autumn (on 12 October 2011 -from 8.00 a.m. to 12.00 a.m.- air temperature was 31°C), winter (on 20 January 2012 -from 8.00 a.m. to 12.00 a.m.- air temperature was 18°C) and spring (on 9 May 2012 -from 8.00 a.m. to 12.00 a.m.- air temperature was 43°C) The nine sampling site locations are shown in Fig. 1.

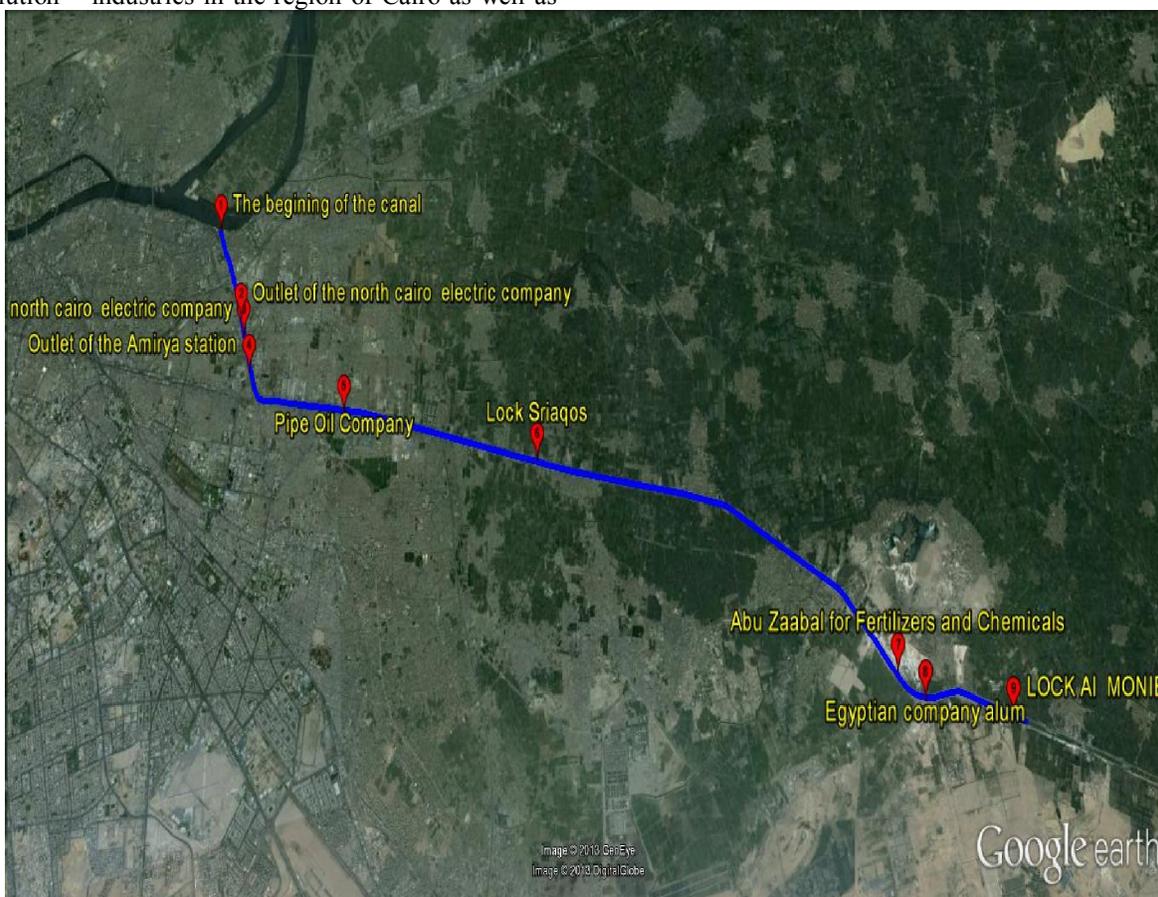


Fig. 1. Sampling locations in Ismailia canal, Egypt.

- 1-The beginning of the canal
- 2- Inlet of the north Cairo electric company
- 3-outlet of north Cairo electric company
- 4-outlet of the Amirya station
- 5- Outlet of petroleum companies
- 6-lock Sriaqos(500 m after petroleum companies)
- 7-Abu zaabal for fertilizers and chemicals
- 8-The Egyptian company alum
- 9-lock El Munaiyar (1000 m after Egyptian company alum)

**Sample extraction**

After returning to the laboratory, aliquots of given samples (1.0 L) were filtered through a 0.45  $\mu\text{m}$  microporous filter membrane under vacuum in order to remove algae, zooplankton and suspended particles. A measured aliquots of an internal standard mixture containing naphthalene-d8, acenaphthene-d10, phenanthrene-d10 and chrysene-d12 was added to each sample. The extraction of the samples was carried out by liquid – liquid extraction method (LLE) [12]. The apparatus for this consisted of 2000 ml volume separating funnel mounted on a retort stand. The separating funnel was thoroughly washed and dried over night in a muffle furnace at an elevated temperature. Prior to use the funnel was rinsed vigorously with acetone then with hexane for several minutes. This was removed and allowed to dry. 1 L of water sample to be extracted was transferred to the separating funnel. Rinse the sample bottle with three 20 ml portions of hexane, transferring each rinsing to the separating funnel. This was shaken vigorously for 2 min and allowed to separate and settle for a minimum of 5 minutes. Assemble a drying funnel containing glass wool and 30 grams of sodium sulfate anhydrous. Rinse with three 10 ml portions of hexane, discarding these rinses. Drain the extract through the sodium sulfate drying into 500 ml boiling flask. Repeat the extraction process with the aqueous layer two more times with 60 ml of hexane each time. Drain hexane extract through same drying funnel collecting in the same boiling flask. Rinse the drying funnel with 30 ml hexane, collecting all washings in the same boiling

flask. Evaporate the extract to approximately 5 ml using a rotary evaporator, add 30 ml toluene and concentrate extract to approximately 1ml using stream of clean nitrogen gas. The extract is ready for GC-FID analysis.

**Sample Analysis****GC-FID analysis**

Chromatographic analyses were carried out with Agilent technologies 7809 gas chromatograph GC, equipped with a flame ionization detector (FID). The column used was a HP5 (30 m x 0.25 mm i.d x 0.25  $\mu\text{m}$  film thickness). The carrier gas was Helium at a flow rate of 1.6 mL/min. Injections were made in the splitless mode at an injector temperature of 300 °C. The detector temperature was set at 300 °C. The temperature program employed was: initial oven temperature at 85 °C increasing at 4.6 °C/min up to 300 °C, stable at 140 °C for 2 min, then at 4 °C/min up to 225 °C and kept constant until the end of program. The total run time was 55 minutes. The sample volume injected was 1  $\mu\text{L}$ . For detection, peaks interfere were compared to the standard and from peak area, recovery value was calculated for spiked sample [13].

**3. Results and discussions****PAHs concentrations and compositional patterns**

The total PAHs concentrations ranged from 697 to 13170 ng/L in water samples collected from Ismailia canal (Tables 1 and 2). The highest PAHs concentrations observed in summer samples and the lowest PAHs concentrations observed in winter samples.

Table 1: Concentrations range of PAHs in water samples in summer and autumn collected from Ismailia canal, Egypt

Compound	PAHs in Summer ng/l				PAHs in Autumn ng/l			
	Range	Mean	±SD	Range	Mean	±SD		
Naphthalene	58	1195	559	±398.57	32	350	162	±101.3
Acenaphthylene	70	860	270	±231.03	ND	165	70	±71.58
Acenaphthene	ND	1212	500	±381.35	ND	476	122	±184.6
Fluorene	27	676	327	±201.24	22	365	122	±107.5
Phenanthrene	104	734	498	±234.68	104	382	260	±116.6
Anthracene	20	715	64	±74.35	10	265	83	±77.04
Fluoranthene	49	1164	119	±62.76	ND	365	64	±51.19
Pyrene	18	803	57	±74.85	ND	653	38	±49.15
Benzo(a)anthracene	ND	732	73	±94.38	ND	154	0	±52.97
Chrysene	ND	617	61	±143.94	ND	270	123	±122.5
Benzo(b)fluoranthene	21	592	53	±31.57	29	365	54	±30.02
Benzo(k)fluoranthene	22	756	61	±32.20	ND	185	93	±64.37
Benzo(a)pyrene	27	828	85	±119.30	ND	230	48	±44.90
Dibenzo(a,h)anthracene	ND	829	53	±29.05	ND	370	20	±61.77
Indeno(1,2,3-cd)pyrene	ND	788	29	±29.98	12	130	24	±23.14
Benzo(ghi)perylene	ND	669	2	±26.77	ND	492	19	±19.28
<b>ΣPAHs</b>	<b>1055</b>	<b>13170</b>			<b>777</b>	<b>5217</b>		

Table 2: Concentrations range of PAHs in water samples in spring and winter collected from Ismailia canal, Egypt.

Compound	PAHs in spring ng/L			PAHs in winter ng/L				
	Range	Mean	±SD	Range	Mean	±SD		
Naphthalene	50	394	270	±129.41	11	350	176	±99.25
Acenaphthylene	9	243	103	±70.97	16	165	123	±91.61
Acenaphthene	ND	598	125	±206.03	ND	476	131	±79.19
Fluorene	ND	398	178	±134.93	22	365	258	±235.7
Phenanthrene	57	405	376	±205.10	128	382	466	±228.6
Anthracene	13	390	45	±65.04	18	265	140	±123.5
Fluoranthene	ND	572	80	±57.63	ND	365	114	±58.92
Pyrene	ND	456	56	±54.15	ND	653	86	±64.89
Benzo(a)anthracene	ND	367	22	±62.45	ND	154	42	±58.10
Chrysene	ND	365	65	±93.51	13	270	86	±40.97
Benzo(b)fluoranthene	37	176	76	±39.14	ND	365	43	±45.55
Benzo(k)fluoranthene	ND	298	53	±65.58	12	185	37	±34.28
Benzo(a)pyrene	ND	198	65	±60.79	ND	230	23	±68.08
Dibenzo(a,h)anthracene	ND	390	63	±31.36	ND	370	0	±56.44
Indeno(1,2,3-cd)pyrene	ND	240	0	±14.40	ND	130	24	±38.27
Benzo(ghi)perylene	ND	470	20	±27.15	ND	492	7	±36.65
<b>ΣPAHs</b>	<b>871</b>	<b>5960</b>			<b>719</b>	<b>5217</b>		

### Concentrations of PAHs in water samples

The total PAHs concentrations in summer, autumn, spring, and winter samples ranged from 1822 to 13170 ng/L, 866 to 5217 ng/L, 697 to 5960 ng/L, 926 to 5217 ng/L respectively (Figure 2). The highest concentration of all samples observed at location 5, which is represented the outlet of petroleum companies, due to the excess amounts of oils and petroleum wastes that is important sources of PAHs discharged from this companies into the canal.

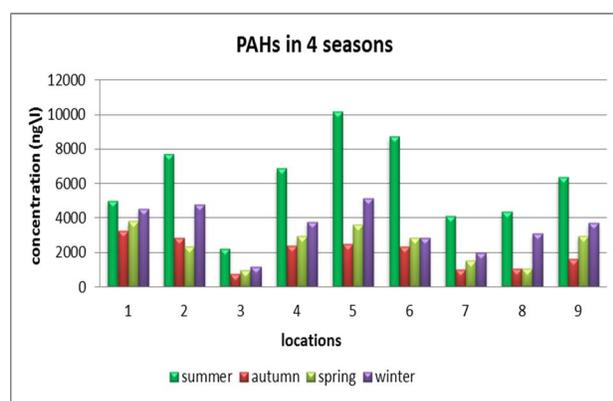


Figure 2, Concentrations of PAHs in all samples collected from Ismailia canal during four seasons.

### Distribution of PAHs in Ismailia canal

The compositional pattern of PAHs by ring size along the contamination gradient is shown in figures 3, 4, 5, and 6. It is clear that two- and three-ring PAHs

(naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene) are the most abundant PAHs, which on average occupied 19 and 59% of total PAHs in summer samples and 12 and 50% of total PAHs in autumn samples. In addition, four- and five-rings PAHs on average occupied 13 and 16% of total PAHs in spring and 18 and 5% of total PAHs in winter, respectively.

The total PAHs concentrations in summer samples ranged from 1822 to 13170 ng/L, (Table 1). The highest concentration of summer samples observed at location 5 (Figure 3), which is represented the outlet of petroleum companies, due to the excess amounts of oils

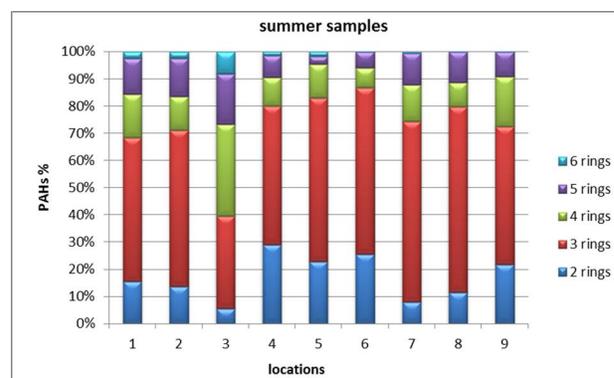
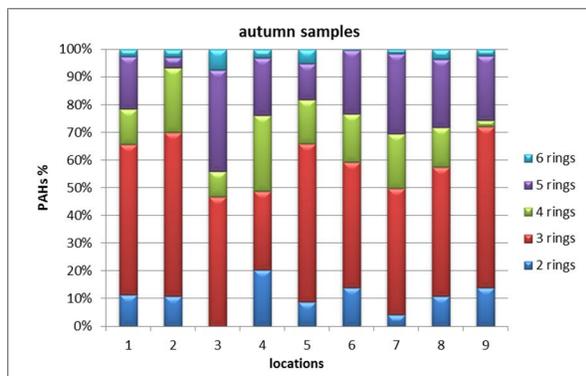


Figure 3, Composition pattern of parent PAHs in summer samples from Ismailia canal.



**Figure 4.** Composition pattern of parent PAHs in autumn samples from Ismailia canal.

The total PAHs concentrations in autumn samples ranged from 866 to 5217 ng/L, (Table 1). The highest concentration of autumn samples observed at location 2 (Figure 4), which is represented the outlet of north Cairo electrical company, suggesting sewage discharges from this company on the canal is important sources of PAHs.

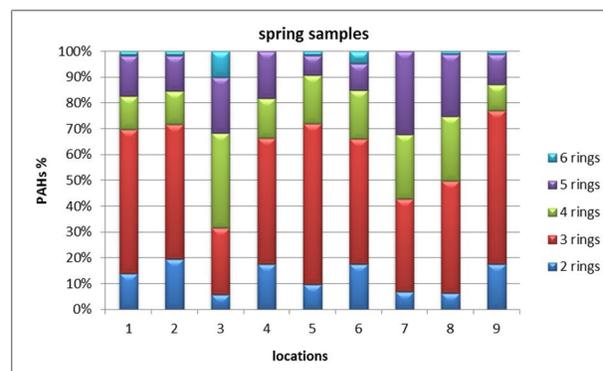
The total PAHs concentrations in spring samples ranged from 697 to 5960 ng/L (Table 2). The highest concentration of spring samples observed at location 5 (Figure 5), which is represented the outlet of petroleum companies, due to the excess amounts of oils and petroleum wastes that is important sources of PAHs discharged from this companies into the canal.

The total PAHs concentrations in winter samples ranged from 926 to 5217 ng/L (Table 2). The highest concentration of winter samples observed at location 5 (Figure 6), which is represented the outlet of petroleum companies, due to the excess amounts of oils and petroleum wastes that is important sources of PAHs discharged from this companies into the canal.

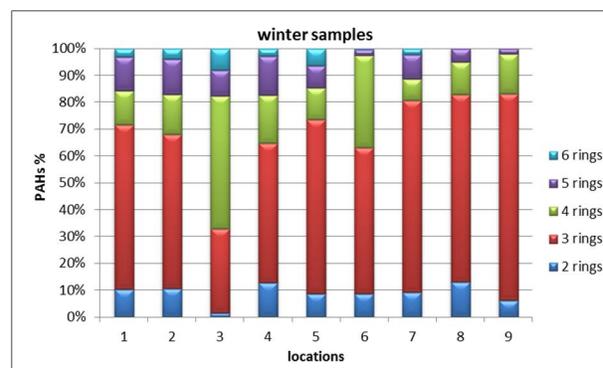
#### Sources of PAHs

Parent PAHs have both natural sources (such as oil seeps, bitumen, coal, plant debris, forest and Prairie fires) and anthropogenic sources (such as fossil fuels and combustion). Since the PAH compositions of the two sources overlap, the significance of anthropogenic PAHs in the environment must be evaluated against a dynamic background of natural PAHs. However, in many areas affected by human activities, natural sources of PAHs, except perylene are overwhelmed by anthropogenic sources. Anthropogenic sources include both high and low temperature combustion of fossil fuels and the direct release of oil and oil-products. For parent PAHs, combustion and/or anthropogenic input is often inferred from an increase in the proportion of the less stable, "kinetic" PAH isomers relative to the more stable, "thermodynamic" isomers. The stability of the lighter PAH isomers has been calculated to support such interpretations [14]. The ratios of phenanthrene/anthracene (Ph/An) within the three-ring

PAH group and fluoranthene/pyrene (Fl/Py) within four-ring PAH group were used to differentiate PAHs of different origins. Ph is more thermochemically stable than An, and therefore at low maturation temperatures much higher molar fraction of Ph is produced compared to An. These molar ratios of Ph/An at petroleum maturation temperatures lead to higher values. These can be as high as 50 at 373 K. To the contrary, high temperature processes (800–1000 K), such as the incomplete combustion of organic materials (coal burning, wood burning, vehicular exhaust emission, waste crankcase oil and asphalt roofing material), are characterized by low Ph/An ratio value (4–10). Thus,  $Ph/An > 15$  for petrogenic sources and  $Ph/An < 10$  for pyrolytic sources. Due to the wide range of values for this index found in the literature, values between 10 and 15 are considered indeterminate relative to source [ 15,16].



**Figure 5.** Composition pattern of parent PAHs in spring samples from Ismailia canal.



**Figure 6.** Composition pattern of parent PAHs in winter samples from Ismailia canal.

Likewise, discrimination also occurs in the fluoranthene/pyrene (Fl/Py) ratio. In petroleum-derived PAHs, pyrene is more abundant than fluoranthene. At higher combustion temperatures a predominance of fluoranthene over pyrene is characteristic. As such, a value greater than 1 is classically related to pyrogenic sources [17]. Hence, in combination, a Ph/An ratio

value <10 and Fl/Py ratio >1 indicates that PAHs originate from pyrogenic sources [15]. The ratios of Ph/An and Fl/Py in summer, autumn, spring, and winter were calculated and are listed in Tables 3 and 4. As shown in Tables 3 and 4, the ratios of Ph/An > 15

and Fl/Py < 1 in locations 4, 5, and 6 which tended to indicate that PAHs were coming from petrogenic sources. But the ratios of Ph/An < 15 and Fl/Py > 1 in locations 1, 2, 3, 7, 8, and 9 which tended to indicate that PAHs were coming from pyrogenic sources.

Table 3, Ratios of phenanthrene/anthracene (Ph/An), fluoranthene/pyrene (Fl/Py) in summer and autumn samples.

Summer samples			Autumn samples		
locations	Ph/An	Fl/Py	locations	Ph/An	Fl/Py
1	2.14	3.4	1	1.44	4.17
2	2.49	3.5	2	2.47	1.56
3	2.08	2.88	3	6.13	ND
4	16.95	0.76	4	15	0.45
5	22.09	0.66	5	16.88	0.40
6	18.19	0.78	6	15.25	0.87
7	8.31	2.7	7	1.6	3
8	3.1	2.08	8	1.59	ND
9	4.53	1.22	9	3.20	ND

Table 4, Ratios of phenanthrene/anthracene (Ph/An), fluoranthene/pyrene (Fl/Py) in spring and winter samples.

Spring samples			Winter samples		
locations	Ph/An	Fl/Py	locations	Ph/An	Fl/Py
1	2.11	1.4	1	2.21	1.6
2	1.25	ND	2	1.52	5.69
3	2.9	1.5	3	4.38	4.53
4	15.76	0.08	4	15.88	0.79
5	17.17	0.37	5	16.94	0.57
6	15.82	0.87	6	16.44	0.61
7	1.98	3.4	7	1.44	ND
8	4.38	4.53	8	2.26	3.14
9	2.45	2.04	9	4.94	1.55

## Conclusion

For the water samples investigated in Ismalia canal, the concentrations of total PAHs at all stations are lower than 10000 ng/L. Consequently, water borne PAHs alone may not be present at levels to cause acute toxicity to certain exposed organisms. The two- and three-ring PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene) are the most abundant PAHs in the study area. The PAHs in water samples originated mainly from petrogenic inputs based on the high proportion of two-ring (naphthalene) and three ring PAHs. Oil spill and industrial wastewater might be important sources.

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