RESEARCH ARTICLE

Environmental carcinogenic polycyclic aromatic hydrocarbons (PAHs): concentrations, sources and hazard effects

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) and their nitrated derivatives are common contaminants that are difficult to be biodegraded in the environment. Many of these compounds are highly carcinogenic and/or endocrine disrupting at relatively low levels.

This report presents the profile of PAHs and selected nitrated derivatives NPAHs such as 1-nitropyrene (1-NP) and 6-nitrocrysene (6-NC) and their major contributors (sources) in air and water environment (first time to discuss NPAHs not only in Egypt but in all Africa environment). Eighteen grape water samples were collected from 3 different sites along the River Nile from North to south in winter season. Beside, fourteen air samples were collected from two different (traffic and industrial) sites. These sites were selected to represent the different parts with the different activities and the distribution levels of PAHs and their nitrated derivatives in Egypt environment. The concentrations of fifteen PAHs having two to six rings were determined by using HPLC with florescence detection, while the concentrations of two NPAHs, 1-NP and 6-NC, were determined using HPLC with chemilumencence detection. The investigated concentration values of total average PAHs and NPAHs in River Nile water samples the PAHs and NPAHs concentration values in winter season were ranged from 1.2 to 3.5 µg/l and from 4.7 to 11.3 ng/l, respectively. While in the atmospheric samples in winter season were ranged from 42.9 to 71.2 Pmol/m^3 and from 52.0 to 64.2 fmol/ m^3 respectively.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are produced in the atmosphere as by-products of the incomplete combustion of almost any fuel. Therefore, they are ubiquitous in the environment, mainly close to urban or industrialized areas (Brown et al., 1996, Mastral and Callen, 2000; Rehwagen et al., 2005; Nassar et al 2012; Li et al., 2012) and have started to be widely studied with regard to their environmental effects due to their well-known carcinogenic and mutagenic properties (Williams, 1990). Once emitted, PAHs will be redistributed between gas and particle phases and removed from the atmosphere and deposited on the earth surface. The atmospheric input of semivolatile organic compounds (SVOCs) to the aquatic environment has been investigated since the early 1970s

(Bidleman and Olney, 1974). The atmospheric concentration levels PAHs and NPAHs were found to be highly correlated with the traffic volume (Hayakawa et al., 1995; Kakimoto et al., 2000).

Although PAHs could travel over long distances and be deposited to the more remote areas, the highest deposition fluxes were monitored in the vicinity of urban and industrial areas (Halsall et al., 1997; Ollivon et al., 2002). However, work on the effects of atmospheric PAH deposition on water bodies in urban areas is scarce. An urban lake, not only provides habitats for a wide variety of wildlife, such as water birds and fishes, but also provides other important ecological services, including aquaculture and aesthetic value. In view of their semi-enclosed character and hydrology, urban lakes are vulnerable to the accumulation of SVOCs, such as PAHs and NPAHs (Nassar 2011).

PAHs are emitted into the atmosphere by various combustion sources (Sicre et al., 1987; Fernandes and Brooks, 2003; Nassar et al 2011) or released in the aquatic environment through the discharges from human activities such as industrial or domestic sewage effluents (Neff, 1979; Burgess et al., 2003). Petrogenic and pyrogenic PAHs have different environmental availability, which is reflected in different responses to microbial degradation (Gwschend and Hites, 1981) or uptake by biota (Farrington et al., 1983). In aquatic systems, PAHs partition between truly dissolved, colloidal and particulate phases, which subsequently influences their mobility and availability in watersheds (Laor et al., 1999; Abdel Gawad et al., 2014; Nassar et al., 2015). Because these non-polar contaminants have low water solubility, they are primarily associated to particles. Their mobility between phases depends not only on intrinsic physico-chemical properties of individual compounds (e.g., solubility, vapour pressure) (Zhou et al., 1998) but also relies on environmental variables such as the amount of rainfall and morphological characteristics of drainage basins (Milliman, 2001).

Egypt is growing not only in population and number of vehicles but also in industrial activities. Urbanization and industrialization have increased very rapidly in Egypt, particularly in the second half of the last century, causing an increase in the pollution of its air-water environment. The majority of these industrial facilities are distributed to the north and south of Egypt, because these areas have available space, and close to the River Nile (El Dars et al., 2004). The River Nile is the principal fresh water resource for Egypt; the Nile also is a primary receptor of wastewater and irrigation return flow. The availability of water of acceptable quality in Egypt is limited and getting even more restricted, while at the same time, the needs for water increase as a result of population growth, industrial development and cultivation of desert land. Egyptian industry uses $638 Mm^3 yr^{-1}$ of water, of which $549 Mm^3 yr^{-1}$ are discharged to the drainage system. The River Nile supplies 65% of the industrial water needs and receives more than 57% of its effluents (Wahaab and Badawy, 2004).

Egypt depends on Nile River transportation for many inert materials like sulpher, phosphate and iron, moreover, the transportation of oil and its products from north to south (EEAA, 2005).

More than 95% of Egyptian water resources come from River Nile whose quality, however, dramatically worsened in the past few years because of pollution due to growing industrialization. In Egypt there are no national monitoring program concerning the identification and determination of organic micro pollutants in drinking water resources. Few studies were carried to measure the concentration of pesticide in aquatic environment (Badawy, 1989; Barakat, 2004; Nassar et al., 2015).

In this report, PAHs and some NPAHs (1-NP and 6-NC are considered to be the primary and major indicators of NPAHs) were sampled from air and water environment in Egypt. The purpose of this work is to (i) to investigate the water and air concentration levels of PAHs, NPAHs at the designed sampling sites, (ii) to identify the major sources of PAHs and NPAHs in Egypt. These results should contribute to the global database on PAHs and NPAHs as well as for regulatory action to improve air-water environmental quality in Egypt.

Experimental

Sampling sites description

Water sampling sites

The distribution of PAHs along River Nile system, which forms the main water source of Egypt, was investigated. Three sites were selected to represent different sectors in River Nile. These sites are El Ayat (Upper Egypt) in Giza governorate at the south part of River Nile. This site represents mainly residential area. Second site is Shobra located in Cairo governorate, at this location the electrical power station, ship maintenance center and Nile transportation and some industrial facilities are discharging their wastewater into the River. In addition to that site is considered downstream of most Greater Cairo activities. The last site is kalyob (North Egypt) in Kalyobeya governorate at the Northern part of River Nile at the beginning of Delta area (Fig. 1A).

Air sampling sites

The population in Greater Cairo exceeds 15 million concentrated over an area of about $214 km^2$ (almost 4.2 km wide and 50 km along the Nile River). Cairo has had a dramatic growth in the number of vehicles, where there are over

2,000,000 cars on the streets of Cairo, 60% of which are over 10 years old, the fuels used in Cairo are mainly unleaded gasoline and diesel, and some vehicles use compressed natural gas (CNG) (Khoder, 2007). Therefore, they lack modern emission cutting features like catalytic converters.

Two sites within Greater Cairo were selected for air borne particulate sampling to represent the different sectors in Greater Cairo. The classification of these sites according to the main activity of both sites. Site 1 (El Haram) is in an urban area located south west of the Cairo city center; it is characterized by heavy traffic and various activities yielding air pollutants. Site 2 (Helwan) is about 22 km south of Central Cairo, in a heavy industrial area. The most important factories in this area are steel, cement, chemical, fertilizer, brick and car industries. Currently, Egypt is ranked 65 among world steel producers as per the World Steel Institute with total production of 4.5 million tons per year, representing about three quarters of Egypt total annual consumption (6 million tons). In addition, Greater Cairo coal production is reported to be around 360,000 tons per year, and this contributes to a national demand for hard coal of around 1.2 million tons per year, which is primarily for the Helwan steel works. There are more than 27,000 registered factories in Greater Cairo, representing more than 40% of the national total (CAPMAS-b, 1997, vol. 2, SA7, P 18). Between 1986 and 1996, gross domestic product (GDP) of Egypt increased by 118%, while Greater Cairo's share of the GDP increased from 42.4 to 50.1% during this period (Rodenbeck, 2000) (Fig. 1B).

Chemicals

EPA610 PAH Mixture containing : naphthalene (Nap), acenaphthalene (Ace), fluorine (Fle), anthracene (Ant), phenanthrene (Phe), fluoranthene (Flu), pyrene (Pyr), benz[*a*]anthacene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenz[*a,h*]anthracene (DBA), benzo[*ghi*]perylene (BghiPe) and indo[*1,2,3-cd*]pyrene (IDP) were purchased as PAH standard solution from Supleco (Bellefonte, PA, U.S.A). Five deuterated PAHs (Nap-d_8, Ace- d_{10}, Phe-d_{10}, Pyr-d_{10} and BaP-d_{12}) were purchased from Wako Pure Chemical (Osaka, Japan) as internal standards and they were dissolved in acetonitrile (Kanto Chemical, Tokyo, Japan). While 1-nitropyrene (1-NP) and 2-fluoro-7-nitrofluorene (FNF, internal standard) were purchased from Aldrich (Chemical) (Milwaukee, WI, U.S.A.) and 6-nitrochrysene (6-NC) was kindly provided by Dr. Nobuyuki Sera of Fukuoka Institute of Health and Environmental Science (Fukuoka, Japan). All other chemicals used were of analytical-reagent grade.

Sampling and extraction

For water samples narrow neck glass bottles (previously washed with dichloromethane) were used to collect two liters water samples from three different sites along the River Nile (Shobra RN1, El Ayat RN2 and Kalyob RN3). The samples were filtered through glass fiber filter paper (GC-50) followed by 3M embore discs filtration (C18), then we extract both filters separately. C18 discs were extracted using dichloromethane followed by super sonication twice, filtration through 0.45 µm poor size glass filter paper, then addition of 100 µm DMSO, evaporation followed by dissolving in 900 µl ethanol and then evaporation Finally, the sample solution was filtered through a membrane filter (HLC-DISK13). Other conditions were the same as in our previous paper, while we apply the same liquid-liquid extraction technique for the GC-50 filter paper as we did for the atmospheric samples.

The atmospheric samples were collected by using high volume air sampler equipped with a quartz filter paper at two sites within the Greater Cairo (El Haram and Helwan) from December 25 to January 7, 2014 at a flow rate of 1,100 l/min. The filters were replaced every 24 hours. The filters containing airborne particulate matter were cut into small pieces (5mm square) and put in a glass flask, then added with 100 µl internal standards and benzene/ethanol (3:1 v/v), then supersonicated for 15 minutes. This step was carried out twice using new benzene/ethanol each. The extracted solution was filtered through a paper filter (Toyo No.6, 125 mm diameter, Toyo Roshi., Tokyo Japan) and a membrane filter (Kanto Chemical HLC-DISK13, diameter 13 mm, pore size 0.45 µm). Then a washing step was carried out using 5% (w/v) sodium hydroxide solution, 20% (v/v) sulfuric acid solution and distilled water successively. After adding 100µl dimethyl sulfoxide (DMSO), rotary vaporization was carried out till dryness. Then the precipitate was dissolved into 900-µl ethanol. Finally, the sample solution was filtered through a membrane filter (HLC-DISK13). Other conditions were the same as in our previous paper (Hattori et al., 2007).

Analysis

The extracted fifteen PAHs from air and water samples were analyzed by using HPLC with fluorescence detection; the system consisted of tow HPLC pumps (LC-10A, Shimadzu, Kyoto, Japan), a fluorescence detector (RF-10A, Shimadzu), a system controller (SCL-10A, Shimadzu), an integrator (Chromatopac C-R7Ae, Shimadzu), a degasser (DGU-14A, Shimadzu), an auto sample injector (SIL-10A, Shimadzu), a column oven (CTO-10AS, Shimadzu), a guard column (Inertsil ODS-P, 4.0 i.d. x 10 mm, GL Sciences Inc., Tokyo, Japan) and an analytical column (Inertsil ODS-P, 4.6 i.d. x 250 mm, GL Sciences Inc., Tokyo, Japan). The mobile phase was a mixture of acetonitrile and

water with a gradient concentration mode of acetonitrile. The flow rate was 1 ml min^{-1}. The time program of the fluorescence detector was set to detect at optimum excitation and emission wavelength for each PAH.

1-Nitopyrene (1-NP) and 6-nitrochrysene (6-NC) were analyzed by using HPLC with chemiluminescence detection with several modifications according to our laboratory detection method. The HPLC system consisted of two analytical columns (both Cosmosil 5C18-MS, 4.6 i.d. x 10 mm, Nacalai Tesque, Kyoto, Japan), two mobile phase pumps (LC-10A, Shimadzu, Kyoto, Japan), a chemiluminescence reagent solution pump (DMX-2000, Sanuki, Tokyo, Japan), a chemiluminescence detector (CLD-10A, Shimadzu, Kyoto, Japan), a system controller (SCL-10A, Shimadzu, Kyoto, Japan), a chromatopac integrator (C-R4A, Shimadzu, Kyoto, Japan), a degasser (DGU-14A, Shimadzu, Kyoto, Japan), an auto sample injector (SIL-10A, Shimadzu, Kyoto, Japan), a column oven (CTO-10AC, Shimadzu, Kyoto, Japan) and a guard column (Cosmosil 5C18-MS, 4.6 i.d. x 10 mm, Nacalai Tesque, Kyoto, Japan). Other conditions were the same as in our previous paper (Tang et al., 2005; Hattori et al., 2007; Nassar et al., 2011).

Results and discussion
Water PAHs, NPAHs profile
PAHs and NPAHs are produced to the environment by incomplete combustion of organic compounds, and are finally decomposed in the atmosphere or eliminated by wet and dry deposition. Several PAHs have been detected in precipitation (Dickhut and Gustafson,1995; Franz and Eisenreich, 1998), but nitroarenes were not detected, because their concentrations in the environment were much lower than those of PAHs (Murahashi et al., 2000). This is the first report to discuss the NPAHs concentration levels not only in River Nile, Egypt, but also in all Africa Environment.

The importance of River Nile in our life is well known to all Egyptians; it is the main source of our drinking water and all living ecosystems. Hence, the pollution problems regarding the Nile have been the subject of public and research concern due to its negative impact on human health. In this investigation, the presence of polycyclic aromatic hydrocarbons and their nitrated derivatives (NPAHs) in River Nile water in the regions of Shobra RN1, Al Ayat RN2 in the south part of Cairo and Kalyob RN3 in the north part of Cairo (beginning of Delta) districts were examined in addition to the determination of their concentrations, sources and distribution.

The data obtained reveal that all surface water samples are shown to be highly contaminated. This may be attributed to the fact that, the studied region is characterized by high navigational activities including anchorages and sailing of ships whose fueling services and exhausts represent an essential source of pollution (WHO, 2003).

PAHs can be divided according to the number of rings into low (2,3 rings) and high (4,5 and 6 rings) molecular weight PAHs (Rentz et al., 2005). High PAHs are highly mutagenic and carcinogenic, whereas, LPAHs are less mutagenic but can be highly toxic (Shi et al., 2005). In general pyrogenic PAHs are characterized by the dominance of the HPAHs over LPAHs. In contrast petrogenic PAHs are normaly abundant in LPAHs, and are readily modified by weathering or degradation (Wang et al., 1999). Thus all sites were contaminated by both pyrogenic and petrogenic of PAHs. It is worthy to mention that the values obtained cannot be related to the whole volume of water since they represent only the surface part where the pollutants are normally concentrated. The real representative values for the whole bulk of the water may be much lower and hence much less alarming.

In this report the investigated total average PAH concentration values of the eighteen grape water samples collected from three different sites in winter season along the River Nile from North to South (Shobra RN1, Al Ayat RN2 and Kalyob RN3) were 3496.1, 1229.7 and 1912.1 ng/l, respectively, while those for selected NPAHs were 11.3, 5.0 and 4.7 ng/l, respectively, (Figs. 2A and B). The 4-ring PAHs were the predominant compounds at all investigated sites (Table 1). These results showed that RN1 site has higher PAH and NPAH concentration values than both RN2 and RN3 sites, this may be attributed to the different activities with different source origin of pollutants in Greater Cairo. Sources of PAHs and NPAHs for all sites were investigated using molecular indices based on the ratios between low and high molecular weight ones (Magi et al., 2002) as (Flu/Pyr), they were chosen according to their thermodynamic stabilities (Tolosa et al., 2004) and also, mono-NPAH to its parent PAH as [1-NP]/[Pyr] and [6-NC]/[Chr] may distinguish between pyrogenic and petrogenic source origin. (Flu / Pyr) <1 indicates pyrolytic origin while (Flu / Pyr) >1; indicates petrogenic origin of PAHs. Petrogenic contamination is characterized by the predominance of LPAHs, while HPAHs prevail in pyrolytic PAHs (De Luca et al., 2005). For sites RN1 and RN2 the (Flu / Pyr) were 1.6 and 1.3, respectively, (higher than 1) indicating petrogenic origin, while site RN3 have the value of 0.8 (less than 1) indicating a pyrogenic origin, while the [1-NP]/[Pyr] and [6-NC]/[Chr] for all sites were ranged from 0.02 to 0.03, these low values indicating a strong contribution of the pyrogenic sources (Table 2).

Atmospheric PAHs and NPAHs

The atmospheric concentrations of PAHs and NPAHs at both sampling sites were shown in Table 3. The average concentrations of 4-6 ring PAHs and two selected NPAHs (1-NP and 6-NC) over the investigated sites were higher at Helwan than at El Haram, where the PAH concentration values were ranged from 17.4 to 88.2 with an average of 42.9 pmol/m^3 at El Haram and ranged from 27.9 to 147.2 with an average of 71.2 pmol/m^3 at Helwan. While the total average concentrations of NPAHs (1-NP and 6-NC) were ranged from 23.7 to 74.6 with an average value of 52.0 fmol/ m^3 at El Haram and ranged from 25.5 to 111.6 with an average value of 64.2 fmol/m^3 at Helwan in winter season (Figs.4A and B).

The concentrations of the four-ring (Pyr, BaA and Chr), five-ring (BbF, BkF and BaP), and six-ring (BghiPe and IDP) PAHs at Helwan site were higher than those at El Haram site, and the four- ring PAHs were the predominant PAHs at both sites (Fig. 5).

Molecular diagnostic ratios of several PAHs have been used to identify characteristics of their sources such as diesel and gasoline engine vehicles (Rogge et al., 1993). Based on their results, two ratios of [BaA]/[Chr]   and [BghiPe]/[BaP] could distinguish the exhausts from gasoline and diesel. In the present study, the [BaA]/[Chr] and [BghiPe]/[BaP] ratios at Helwan and El Haram sites were ranged from 0.4 to 0.5 and from 0.6 to 1.5, respectively, suggesting a relatively stronger contribution of the gasoline engine vehicles at both sites.

On the other hand, the much lower combustion temperature in coal stoves (approximately 1,100-1,200 $^{\circ}$C) than in diesel engines (approximately 2,700 $^{\circ}$C) was considered as the cause of the lower ratio of mono-NPAH to its parent PAH in coal stoves (Hattori et al., 2007). The contribution of diesel exhaust particulate (DEP) and CEP were estimated from their [1-NP]/[Pyr] ratio. In the present study, the [1-NP]/[Pyr] ratio at El Haram and Helwan sites were ranged from 0.005 to 0.008, while [6-NC]/[Chr] ratios were ranged from 0.001 to 0.003 at both sites, these values may refer to the contribution of open air waste burning, DEP and CEP but in lesser extent to the total concentrations of PAH and NPAH of the Egyptian atmosphere (Table 2).

Environmental risk assessment

Polycyclic aromatic hydrocarbons (PAHs)   and their nitro derivatives may cause DNA damage and cancer. However, the mechanism of such interactions has not been fully understood.

Although BaP is considered the most carcinogenic PAH, other carcinogenic PAH compounds (BaA, BbF, BaP, DPA and IDP) shows toxic and/or carcinogenic effects (Mastral et al., 2003). BaP is one of PAHs that is a byproduct of incomplete combustion or burning of organic (carbon-containing) items. BaP is commonly found with other PAHs is metabolized (chemically modified in the body) in humans and animals to form a number of metabolites that may elicit toxicity. BaP and BaP metabolites can bind to DNA forming a structure called BaP-DNA adducts. The formation of BaP-DNA adducts can interfere with or alter DNA replication (formation of DNA copies during cell division), and may be associated with an increased risk of several forms of cancer. BaP is classified as having a mutagenic mode of action (MOA) for inducing tumor formation, and is thought to require metabolic activation to become carcinogenic (U.S. Environmental Protection Agency, 2005). In this study, The investigated BaP and other carcinogenic PAHs show higher concentration values at the atmospheric sites (Helwan and El Haram) much more than the detected concentrations in the water sites. The concentration level profile of the investigated carcinogenic PAHs were as follow:

Helwan> El Haram> NR1> NR2> NR3 (Fig 6).   This index tries to parameterize the health risk for humans and animals related to ambient PAH expositions.
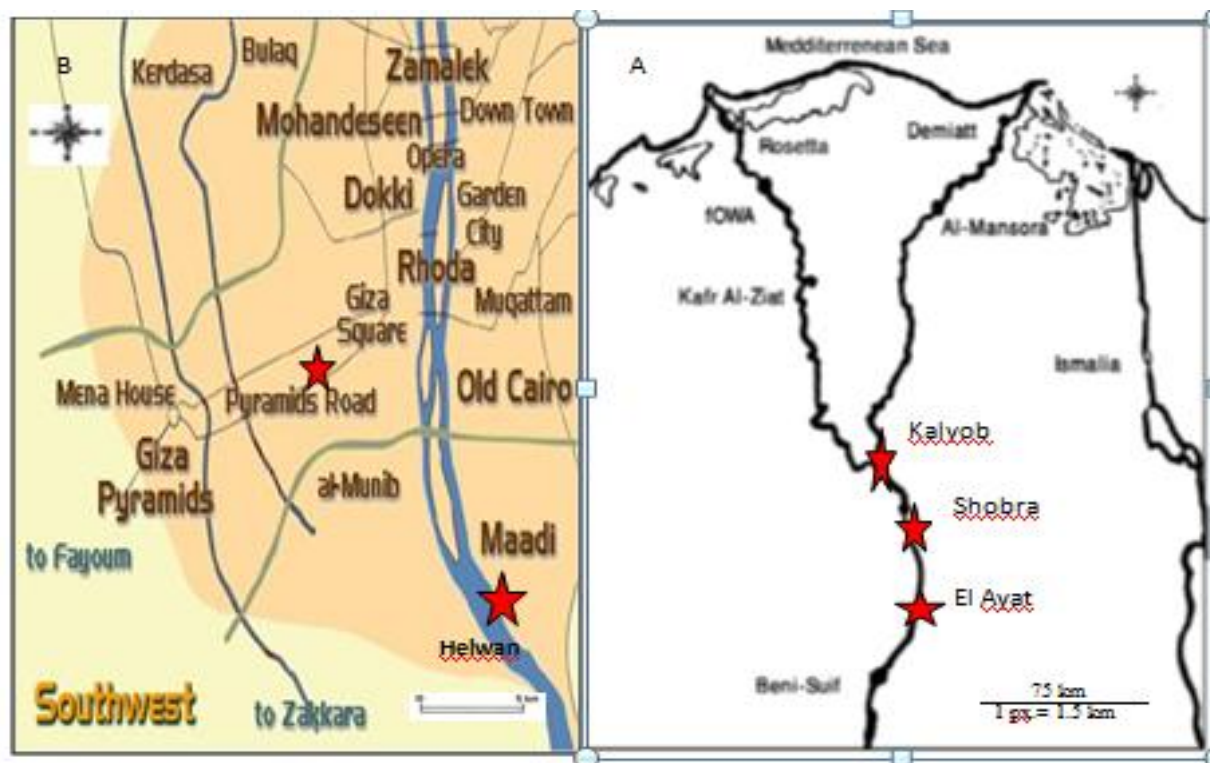
Fig.1. Air and water sampling sites.
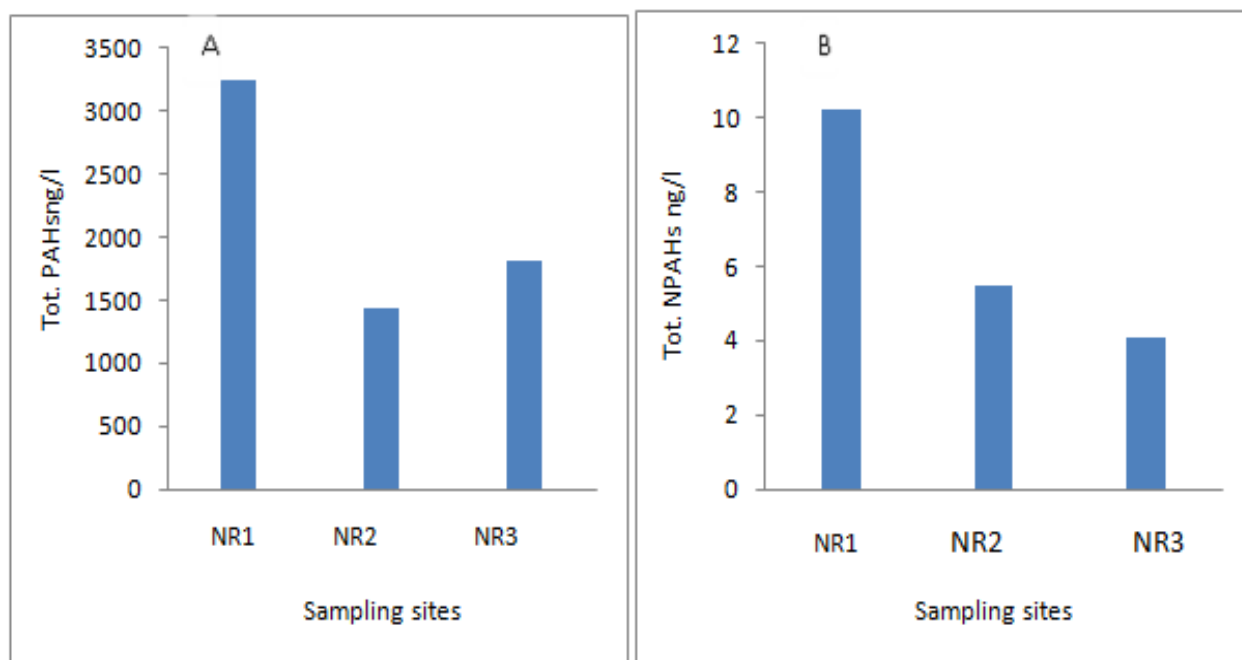

Fig. 2. Total average concentrations of PAHs and NPAHs of Nile River water samples in winter A, Total PAHs (= Nap + Ace + Fle + Phe + Ant +Frt + Pyr + BaA + Chr + BbF + BkF + BaP + DPA + Bghipe + IDP). B, NPAHs (= 1-NP + 6-NC).
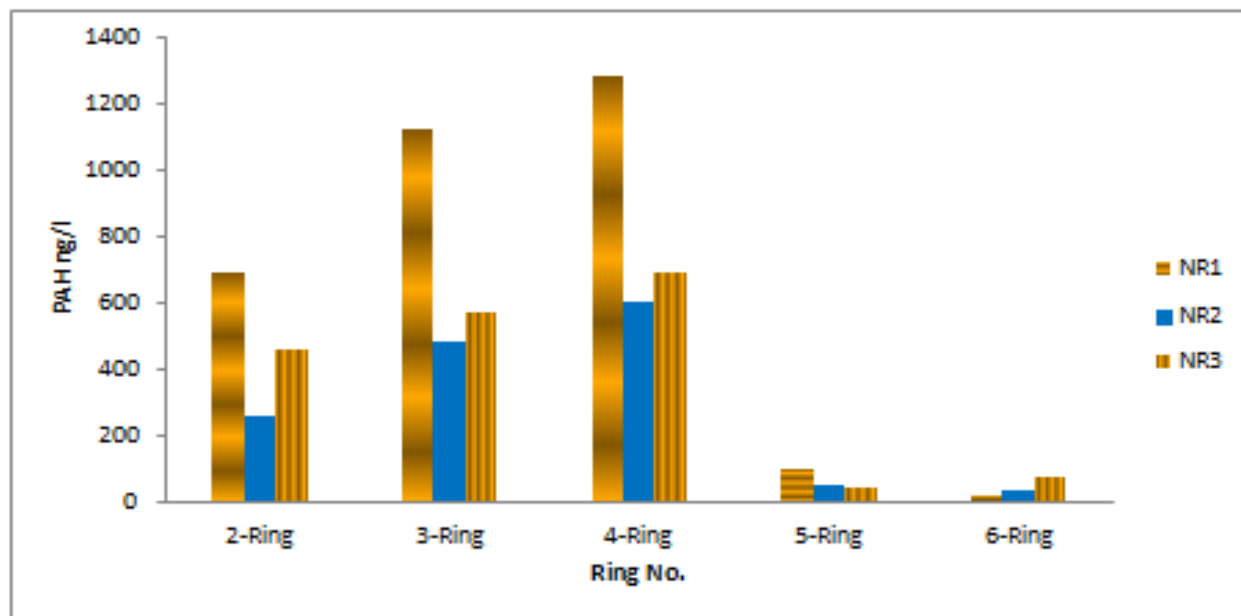
Fig. 3. Distribution of (2-6 ring) PAHs concentration levels in Nile River water samples.
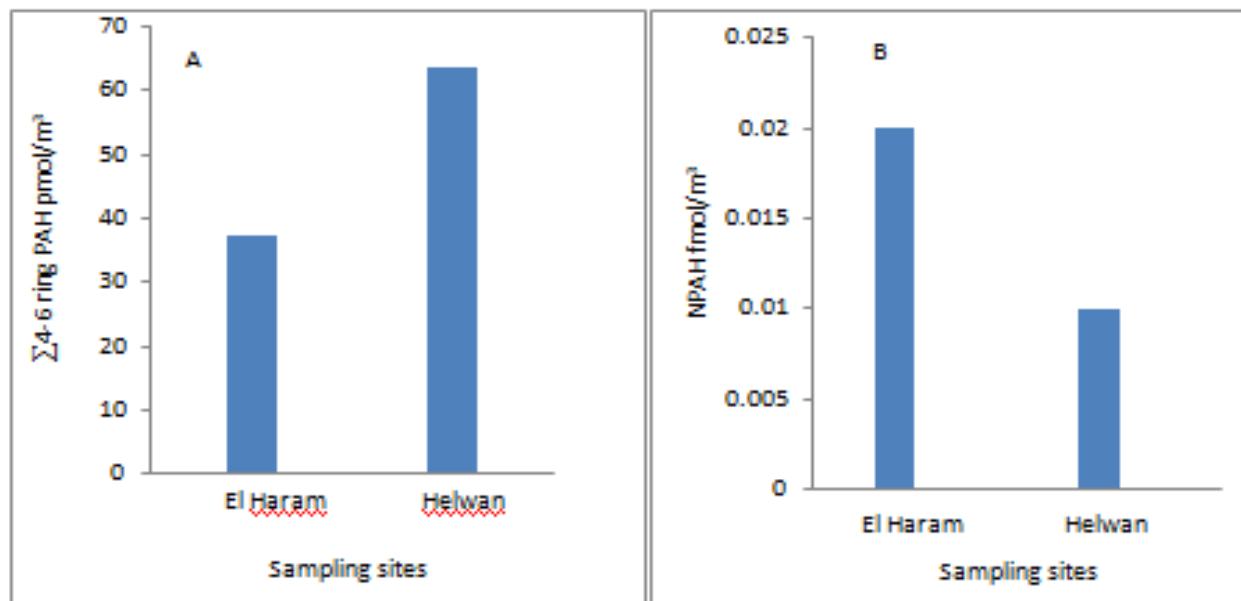
Fig. 4. Total average concentration levels of the atmospheric PAH and NPAH in winter.
A, Total PAHs (= Frt + Pyr + BaA + Chr + BbF + BkF + BaP + Bghipe + IDP); B, NPAHs (= 1-NP + 6-NC).

Fig. 5. Distribution of PAH individual concentration values (Pmol/m3) at El Haram and Helwan sites.
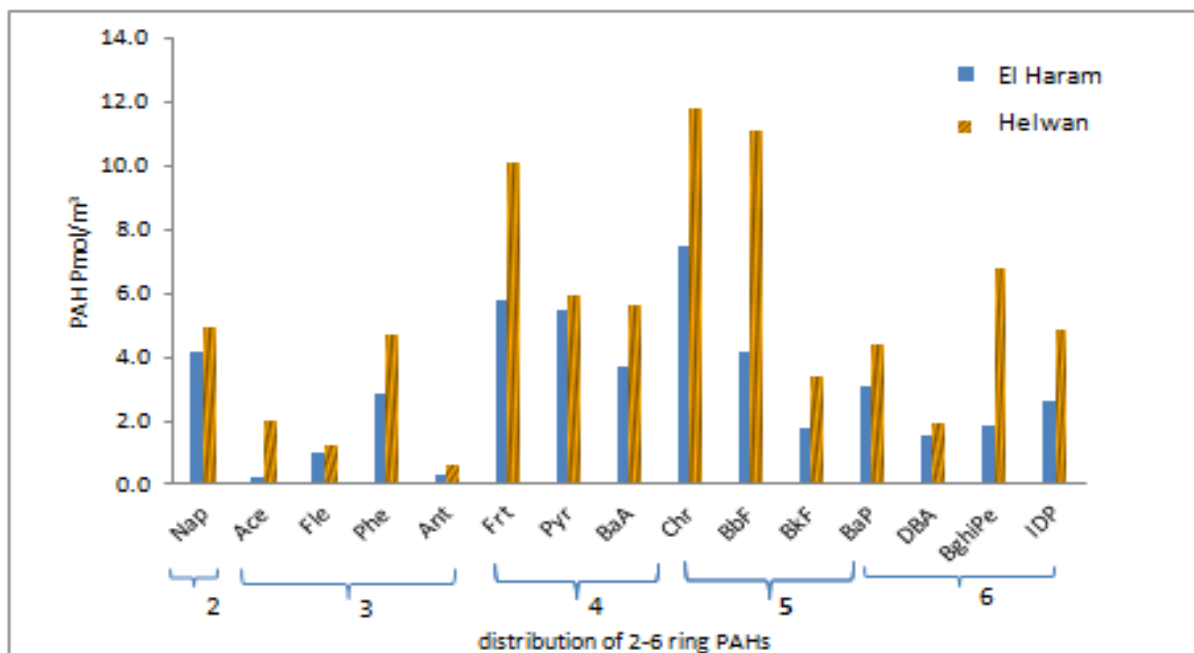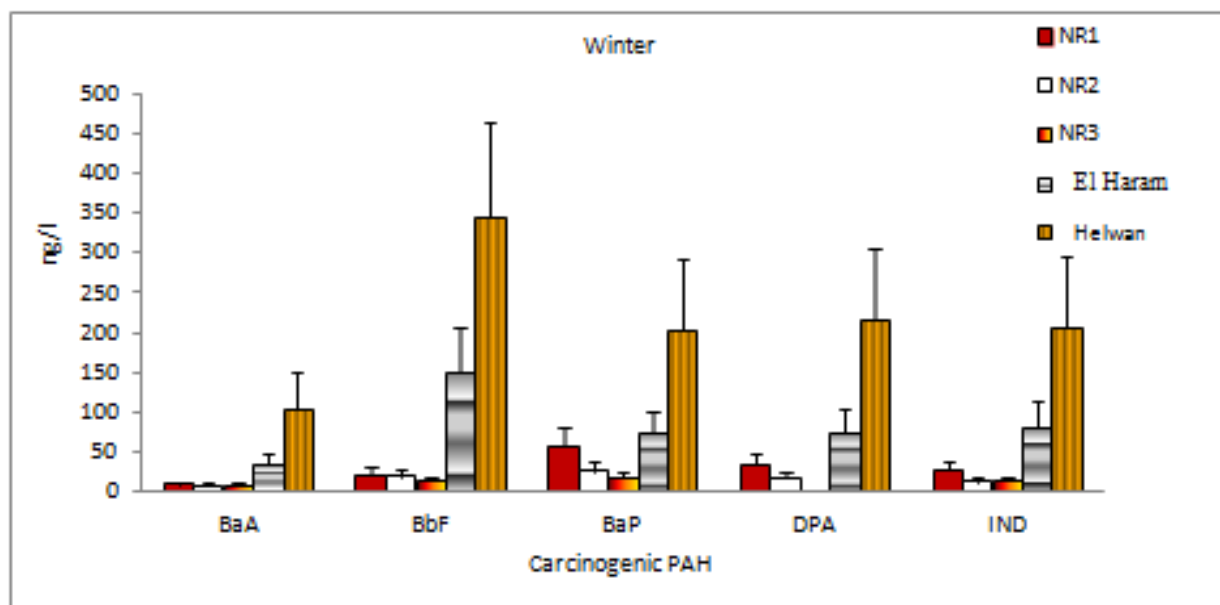

Fig. 6. Concentrations of the individual carcinogenic PAHs at the water and air sampling sites. Each column and vertical bar represent mean values and S.D., respectively.

Table 1
Water PAH and NPAH concentrations at Shobra NR1, El Ayat NR2 and Kalyob NR3 sites in winter

Ring No.	Compound	Shobra NR1				El Ayat NR2				Kalyob NR3	
		Min	Max	Average	STD	Min	Max	Average	STD	Min	Max
	PAH (ng/l)										
2-ring	Nap	132.3	899	700.1	369.8	102	451	281.2	146	81	554
3-ring	Ace	62	298	213.4	109.1	31	156.1	103	45.1	55	161
	Fle	10.2	295.1	159.9	78.5	28.3	214	110.4	81.3	ND	103
	Phe	268.1	1056	740.1	389.1	198.1	650.4	301.5	234.6	100.2	395.1
	Ant	ND	7.1	4.2	2.2	ND	5.8	2.2	1.4	ND	4.8
4-ring	Frt	64.9	615	488.2	248.2	94.2	341.6	211.2	110.5	93.9	265.9
	Pyr	100.2	420	324.8	141	81	233.1	164.5	94.4	109.1	373.2
	BaA	42	342.3	182	119.1	ND	49.6	18.8	13.6	29.8	152.1
	Chr	108.2	405	291.9	136.9	9.1	189.3	122.6	59.8	56.5	182.9
5-ring	BbF	8.6	55.3	24.5	14.2	2.3	18.6	8.3	6.0	1.3	9.4
	BkF	ND	8.3	2.8	2.1	ND	4.8	1.8	1.1	0.5	5.5
	BaP	30.5	95	51.1	29.8	12.2	59.9	31.2	20.2	14.2	7.7
	DBA	9.2	53.5	29.1	18.6	1.2	13.1	5.2	2.9	1.6	8.9
6-ring	BghiPe	2.1	26.3	15.1	9.1	3.5	16.1	9.0	5.2	1.1	16.4
	IDP	ND	17.8	9.2	5.1	4.3	22.4	14	9.2	ND	26.8
	Total (average)	811.2	5079.3	3496.1	1853.1	481.3	2128.3	1229.7	761	1421.2	2177.2
	NPAH (ng/l)										
	1-NP	2.4	14.1	8.1	4.6	0.7	8.1	3.4	2.2	0.4	6.0
	6-NC	0.7	6	3.2	1.4	0.5	4.2	1.5	1.0	0.1	2.1
	Total (average)	3.1	20.1	11.3	6.0	1.2	12.3	4.9	3.2	0.5	8.1

Table 2
Molecular diagnostic indices used to distinguish between the different sources of PAHs and NPAHs in water samples

Molecular indices	NR1	NR2	NR3
[Flu]/[Chr]	1.6	1.3	0.82
[1-NP]/[Pyr]	0.002	0.02	0.01

[6-NC]/[Chr]	0.02	0.012	0.009

Table 3

Atmospheric PAH and NPAH concentration levels at El Haram and Helwan sites in winter

Compound		El Haram				Helwan			
Ring No.		Min	Max	Average	STD	Min	Max	Average	STD
	PAH (pmol/m^3)								
2-ring	Nap	1.78	7.51	5.23	2.32	2.33	12.45	6.12	3.13
3-ring	Ace	0.18	0.42	0.33	0.12	0.37	8.12	3.65	2.41
	Fle	0.41	1.92	1.24	0.65	0.53	4.90	2.11	1.23
	Phe	1.05	4.45	3.34	1.60	1.32	12.42	4.94	3.13
	Ant	0.12	0.91	0.66	0.28	0.02	1.88	0.98	0.50
4-ring	Frt	3.43	17.92	8.65	4.23	1.33	25.15	11.98	7.87
	Pyr	2.62	11.96	6.55	2.93	1.44	13.65	6.34	3.81
	BaA	1.31	7.22	4.16	2.03	1.23	13.23	6.69	3.44
	Chr	2.96	15.12	9.49	4.13	3.77	22.52	11.78	8.21
5-ring	BbF	2.11	7.98	5.19	2.61	3.29	31.12	13.88	8.13
	BkF	0.82	3.96	2.25	1.14	1.14	8.89	4.13	2.25
	BaP	1.65	4.91	4.02	1.90	1.66	8.16	5.12	2.61
	DBA	1.20	2.71	1.84	0.62	1.03	5.91	2.77	1.19
6-ring	BghiPe	0.36	3.43	2.46	1.05	2.42	18.11	8.13	4.29
	IDP	0.25	7.39	3.69	2.22	3.12	8.18	5.65	2.33
	∑4-6 ring PAH (average)	17.42	88.15	42.92	19.82	27.93	147.19	71.23	48.4
	NPAH (fmol/m^3)								
	1-NP	18.73	51.82	37.26	17.19	16.36	82.13	44.35	24.1
	6-NC	4.97	22.86	14.77	8.12	9.18	29.48	19.88	8.87
	Total (average)	23.7	74.68	52.03	25.31	25.54	111.61	64.23	32.9

Nap, naphthalene; Ace, acenaphthalene; Fle, fluorine; Ant, anthracene; Phe, phenanthrene; Frt, fluoranthene; Pyr, pyrene; BaA, benz[*a*]anthacene; Chr, chrysene; BbF, benzo[*b*]fluoranthene; BkF, benzo[*k*]fluoranthene; Bap, benzo[*a*]pyrene; DBA, dibenz[*a,h*]anthracene; BghiPe, benzo[*ghi*]perylene; IDP, indo[*1,2,3-cd*]pyrene.

Table 4

Molecular diagnostic indices used to distinguish between the different sources of PAHs and NPAHs in atmospheric samples

Molecular Indices	Helwan	El Haram
[BaA]/[Chr]	0.41	0.6
[Bghipe]/[Bap]	1.4	0.79

[1-NP]/[Pyr]	0.008	0.005
[6-NC]/[Chr]	0.001	0.003

Conclusions

• Cairo (Shobra) RN1 site has the highest PAH and NPAH concentration values over the other two sites (El Ayat RN2 and Kalyob RN3) in water samples.

• Fifteen PAHs and selected NPAHs (1-NP and 6-NC), were determined at Egypt air and water environment in winter season.

• The mean total concentrations of PAHs and NPAHs were higher at Helwan (an industrial site) than at El Haram (a traffic site) in the atmospheric samples.

• The average concentration values of 1-NP were higher than 6-NC at all investigated sites for air and water samples.

• 4-ring PAHs (Frt, Pyr, BaA and Chr) have the highest concentration levels of both air and water samples.

• The low values (less than 1) of the molecular diagnostic and nitration ratios of [BaA]/[Chr], [BghiPe]/[BaP], [Flu]/[Pyr], [1-NP]/[Pyr], [6-NC]/[Chr] for air and water samples, indicated a relatively stronger contribution of gasoline engine vehicles, open air waste burning and coal exhaust particulate (CEP) in lesser extent to PAH and NPAH source origin.

• The environmental risk hazard in the water sites shows higher values at NR1> NR2> NR3, while those at the atmospheric sites shows Helwan> El Haram.

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