

Polycyclic Aromatic Hydrocarbons in Atmosphere over Greater Cairo, Egypt

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Abstract: Atmospheric particulate matter samples were collected during the period from December 2007 to November 2009 from four sites at Shoubra El-Kheima (north Cairo) and Helwan (south Cairo). The concentration of PAHs was determined using GC technique. Sixteen PAHs were identified and quantified in the atmosphere of investigated sites Shoubra El-Kheima and Helwan including: Naphthalene (NAP), Acenaphthylene (ACY), Acenaphthene (ACE), Phenanthrene (PHE), Fluorine (FLU), Anthracene (ANC), Fluoranthene (FLA), Pyrene (PYR), Benzo(a)anthracene (BaA), Chrysene (CRY), Benzo (b)fluoranthene (BbF), Benzo (k)fluoranthene (BkF), Benzo (a)pyrene (BaP), Dibenzo (a, h)anthracene (DBA), Indeno (1,2,3-c,d)pyrene (IND) and Benzo (ghi) perylene (BgP). The current study indicated that the total average of PAHs over the investigated sites was 141.2, 165.5, 665.8 and 888.3 ng/m³ at site-1 (North Shoubra El-Kheima), site-2 (South Shoubra El-Kheima), site-3 (North Helwan) and site-4 (South Helwan), respectively during 2008. And it was 396.2, 570.0, 649.0 and 852.1, respectively during 2009. On individual scale, PAHs ranged between 0.077 ng/m³ to 308.2 ng/m³ for (NAP) and (DBA), respectively at Shoubra El-Kheima. Meanwhile it ranged between 0.03 ng/m³ to 567.1 ng/m³ for (ACY) and (BkF), respectively at Helwan. The measured data showed that the total carcinogenic content of PAHs (BaA, BbF, BaP, DBA and IND) were ranged from 34.5% to 63.6% of total PAHs. It has been concluded from the diagnostic ratios of the ambient air PAHs concentrations that characterize the anthropogenic emission. Traffic source is the major at atmosphere.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds constituting only carbon and hydrogen, arranged in two or more aromatic rings. They are widely distributed as environmental pollutants and have both anthropogenic and natural sources (Kameda et al. 2005; Xue and Warshawsky 2005). PAHs are semivolatile organic compounds and present in both gaseous and particulate phases in the atmosphere, depending on the vapor pressure of each PAH compound. The partitioning of PAH compounds between the particulate and gaseous phases depends on the atmospheric conditions (ambient temperature, relative humidity), the nature (i.e., origin and properties) of the aerosol, the interactions between the compound and the aerosol, and the overall behavior of the compound in the atmosphere (Pankow 1994; Vardar et al. 2008; Esen et al. 2008).

Most volatile compounds released from combustion process, in general, are either compounds with two or three aromatic rings, released mainly in the gas phase, compounds containing three or more aromatic rings in their structure, associated with PM emission (Mastral et al, 2003). PAHs with four- to six-ring hydrocarbons are generally of pyrogenic origin (Dahle et al, 2003).

The anthropogenic PAHs are emitted from pyrogenic and petrogenic sources. PAHs generated through the combustion of fossil fuel (coal and petroleum) and biomass are pyrogenic, whereas volatilization and emission of unburned fossil fuel (kerosene, gasoline, diesel fuel, lubricating oil, and asphalt) are petrogenic. (Boonyatumanond et al. 2007). Combustion sources include automobiles, power plants, industries, burning coal and petroleum, and waste incinerators. In urban and industrial areas, atmospheric PAHs are almost entirely anthropogenic in origin and are produced by high-temperature reactions, such as incomplete combustion and pyrolysis of fossil fuels and other organic materials containing carbon and hydrogen (Khalili et al. 1995). The major sources of PAHs in urban atmosphere include gasoline and diesel vehicle exhausts, tire wear debris, asphalt particles, resuspended soils, and power plants (Binet et al. 2002; Dyke et al. 2003; Zielinska et al. 2004).

PAHs were identified to be one of the major toxic air pollutants in urban environments. Several PAHs and some of their degradation products are known to have a high carcinogenic, mutagenic, and allergenic potential, posing a threat to human health (Kameda et al. 2005; Xue and Warshawsky 2005).

Most of high molecular weight PAH

compounds are carcinogenic and mutagenic (Xue and Warshawsky 2005). The low molecular weight PAH compounds are considered to be less harmful to human health than high molecular weight PAH compounds (Park et al. 2001). Epidemiological studies have demonstrated that people living in urban areas have an increased risk of lung cancer compared to people living in rural areas due to higher levels of air pollution (Hemminki and Pershagen 1994; Nielsen et al. 1996). To reduce the risk associated with PAHs through source control, identifying the possible sources of atmospheric PAHs is essential. Natural emission sources of PAHs include forest fires and volcanoes (Kim et al. 2003).

The highest concentrations of atmospheric PAHs have been found in urban environments because of their extensive vehicular traffic and poor atmospheric dispersion (Miguel et al. 1998; Kakimoto et al., 2002). Most of the previous studies on PAHs pollutants in Greater Cairo had been focused on their levels and distribution in suspended particulate matter (Hassan 2006), wet deposition (Khoder, 2006), dust deposited on leaves of street trees, and paved street dust (Khoder 2007), road dust (Hassanien and Abdel-latif, 2008) and gas phase in atmospheric particulates (Hassan and Khoder, 2011). Therefore, the main objectives of the present study are (a) beside evaluate the difference of the environmental concentration levels of PAH compounds in atmosphere of Shoubra El-Kheima and Helwan areas at Greater Cairo, (b) to identify the possible sources of atmospheric PAHs based on diagnostic ratios of PAH compounds, and (c) to evaluate health risks associated with inhalation of PAH compounds in the ambient air of the study area.

Kendall et al., (2001) reported that the most abundant PAH in air was BgP followed by BaA and CRY in the urban area of London. While, Park et al., (2001) recorded that the concentrations of these three compounds contribute over 50% of the Σ PAH in the urban area of Texas, USA, the 5 and 6 ring PAHs were predominant in the particulate phase. Higher BaP concentrations of PAHs were obtained for PM especially in winter (Kendall et al., (2001). The major pollutant sources for PM were coal combustion and vehicle emissions. In addition, a survey of PAHs in residential air in Hangzhou, China, was carried out. Air samples were collected from indoor and outdoor environments during both summer and winter and analyzed for the level of 16 PAHs. The results showed that the total PAH contents ranging from 0.425 to 36.2 $\mu\text{g}/\text{m}^3$ (Zhua et al, 2008).

2. Materials and methods

2.1. Greater Cairo description

Greater Cairo (30°08'_N, 31°34'_E) is the most populous region in Africa with about 18 million inhabitants. Geographically, the city is bordered from the east by the Mokattam Hills separating the city from the Eastern Desert and, to the east, the Abu-Rawash Hills and the Western Desert. Meteorologically, the region is a desert with an annual range of precipitation between 22–29 mm and temperatures between 18–45 °C. Winds prevailing in the area take the northern (N, NW and NE) direction 90% of the time for nine months of the year. The average wind speed, in general, increases significantly above 4 m/s during the winter period, which helps to reduce the ambient relative humidity in cooler weather relative to the summer period (Hassanien and Abdel-latif, 2008). About 52% of the industries and about 40% of electrical power stations in Egypt are found in Greater Cairo, besides more than 2 million vehicles are running in the streets of the Greater city, about 60% of which are over 10 years old and therefore lack modern emission cutting features like catalytic converters. The high rate of emission coupled with low wind speeds and the frequent inversions in the area resulted in high local pollution load. Cairo has a very poor dispersion factor because of lack of rain and its layout of tall buildings and narrow streets, which create a bowl effect. Consequently, it is considered one of the most polluted megacities in the world. Vehicle fuels used in Greater Cairo are mainly unleaded gasoline and diesel, and some vehicles are using compressed natural gas (Hassan and Khoder, 2011).

Cairo houses around 50–55% of the national industrial activity, most of which are belonging to the dominant public sector. The majority of these industrial facilities are distributed to the north (Shoubra El Kheima) and south (around Helwan) due to space availability, their close proximity to the Nile and to power generation facilities (El-Dars et al, 2004).

2.2. Description of sampling sites

Four sampling sites were selected located north Shoubra El-Kheima and south Helwan in greater Cairo. Classification of sites, according to the main activity, is shown in Table (1).

2.3. Sampling

Samples were collected from four sites in Shoubra El-Kheima and Helwan Cairo, Egypt (Fig.1) through glass fiber filters of Whatmann GFA type (12 cm in diameter) with 99% collection efficiency (NAS, 1973; Samare et al., 1990) using medium volume samplers. The average rate of sampling is 14–18 L/min. for twenty four hour sampling occurred from 10a.m.–10a.m. biweekly at the investigated

sites starting from December 2007 to November 2009. Samples were collected at a height of about 10m above ground level. Before sampling, the glass fiber filters were impregnated in acetone to remove

all organic compounds for 24h then heated at 400C° for 4h. The cleaned glass fiber filters were stored in a desiccator until sampling (Thrane and Mikalsen, 1981 and Yamasaki et al., 1982).

Table (1): Sampling sites locations and characteristics.

Site No.	Area	Characterization
1	North Shoubra El-Kheima	Residential-agricultural area, located at northern of Shoubra El-Kheima thermal power plant, upwind from the plant.
2	South Shoubra El-Kheima	Industrial area, located at southern of Shoubra El-Kheima thermal power plant, downwind from the plant.
3	North Helwan	Residential area, located at northern of Helwan power plant, upwind from the plant.
4	South Helwan	Industrial-Residential area, located at southern of Helwan power plant, downwind from the plant.

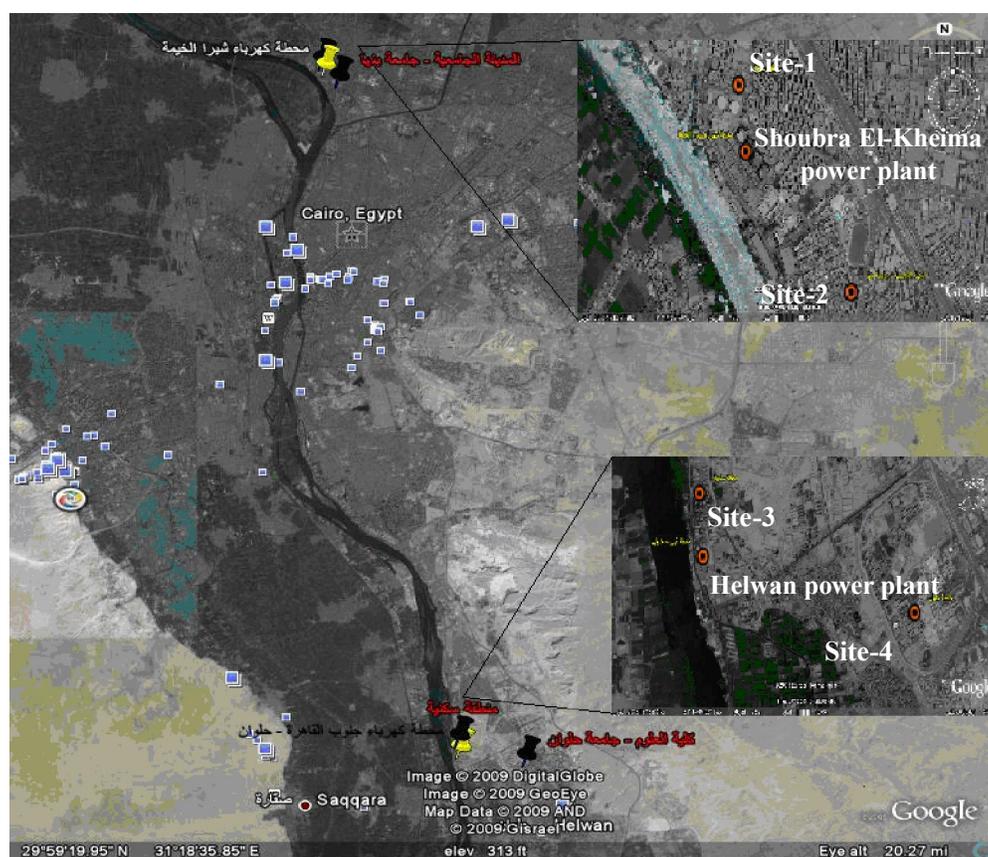


Figure (1): Investigated sites in Shoubra El-Kheima and Helwan areas in Cairo

2.4. Polycyclic aromatic hydrocarbons analysis

Analysis of trace PAHs in environmental samples is an enormously difficult task and even when a large sample is available, a complete analytical resolution of PAHs exceeds the capability of any single analytical technique (Blumer and Giger, 1974). Because a large number of PAHs, including many isomeric ones, are frequently present in air particulate extracts, definitive identification of individual PAHs in such samples may necessitate

combined use of several powerful separation and detection techniques (Choudhury and Bush, 1981). Based on two successive steps, the method used for PAH analysis includes an organic solvent extraction and clean-up procedure. Reagents and solvents used were highly purity Merck grade available.

2.4.1. Analysis

After sampling the filters were dried in a darkened desiccator for 24 h, reweighed until

constant weight to obtain the weight of suspended particulate matter (SPM) using electronic Balance (Swiss quality Precisa model 80A-200M). The weighted filters stored in dark after covered with aluminum foil to protect them from light and kept at 0C° until analyzed to prevent the volatilization of lower molecular weight PAHs (Baek, 1988; Halsall et al., 1993; Allen et al., 1996; Gustafson and Dickhut, 1997). The treatment of the glass fiber filters were recommended by Cretney et al., 1985; Sisovic and Fugas, 1993; Halsall et al., 1994; Manoli and Samara, 1995 and Sisovic et al., 2002; Hassan, 2006).

2.4.2. Extraction and Clean-up

Each filter was then extracted for PAHs analysis as follows: it was putted in glass vial and extracted with 10ml of DCM/n-hexane (1:1) in an ultrasonic bath for 10 min, three times at room temperature. The extract was transferred to a clean vial, and concentrated to about 2ml using rotary evaporator (Iborota 4003 control rotary evaporator with G3 glassware, Heidolph, Germany) (Nielsen, 1996-a, 1996-b; Fromme et al., 1998). The concentrated extracts were fractionated by column chromatography. A column filled with 2 gm anhydrous sodium sulfate and 10 gm silica gel (70 – 230 mesh, ASTM purchased from Merck) to remove water. Silica gel was activated at 120 C° for 8h, 5% of water was added to deactivate the material. The PAH were collected in the second fraction, and were eluted with 20mL of n-hexane/dichloromethane (1:1, v:v). The volumes of the eluates were concentrated using a gentle flow of dry nitrogen gas to a volume of approximately 2ml. The volume was then adjusted to 2ml exactly by addition of dichloromethane reduced to approximately 2ml. This procedure was recommended by (Omar et al, 2002; Sharma et al, 2007; Zhu et al, 2008; Ray et al, 2008; Valavanidis et al, 2008; Zhu et al, 2008; Kobayashi et al, 2008; Lu et al, 2008; Tham et al, 2008; M. Rotatori et al, 2009).

2.4.3. Instrumental analysis

Qualitative and quantitative determinations of individual PAHs were done by Gas chromatograph (GC) with auto-sampler and flame ionization detection (FID) and a split less injection system, as been used by (Benner et al., 1989; Viras et al., 1991; Lee et al., 1995; Khalili et al., 1995; Fertmann et al., 2002; Galarneau et al., 2006 and Wu et al., 2006). Gas chromatography using conventional packed columns can identify the 16 EPA PAHs. So, GC seems to offer the best choice in this regard (Choudhury and Bush, 1981 and Alfheim and Johansen, 1985). In the present study, after

purification, 2 µl of the sample was injected splitless on GC-FID (Model HP 6890), fitted with a Flame Ionization Detector (FID). A HB5 capillary column (30m x 320µm x 0.25µm) was used. The peaks in the chromatogram were identified by comparing retention times (from the GC chromatogram) with those of standards and they were quantified by comparing the integrated peak area with that of the nearest standard, as been recommended by (Möller and Alfheim, 1980; Choudhury and Bush, 1981; Brorström and Lindskog, 1985; Westerholm et al., 1988; Menichini and Monfredini, 1999; Gigliotti, et al., 2000 and Zheng and Fang, 2000). The concentrations of individual PAHs were calculated and expressed in ng/m³. The GC was calibrated with a diluted standard solution of 16 PAH compounds (Supelco, Inc., Bellefonte, PA). The standard PAHs mixture (2000 µg/ml for each) containing: Naphthalene (NAP), Acenaphthylene (ACY), Acenaphthene (ACE), Phenanthrene (PHE), Fluoranthene (FLU), Anthracene (ANC), Fluoranthene (FLA), Pyrene (PYR), Benzo(a)anthracene (BaA), Chrysene (CRY), Benzo (b)fluoranthene (BbF), Benzo (k)fluoranthene (BkF), Benzo (a)pyrene (BaP), Dibenzo (a,h)anthracene (DBA), Indeno (1,2,3-c,d)pyrene (IND) and Benzo (ghi) perylene (BgP) was used for quantification as an external standard, as been recommended by (Re- PoPPI and Silva, 2005).

2.4.4. Detection limit

Several unknown contaminants extracted from glass fiber filters (GF) were effectively eliminated through the extraction procedure and the column chromatography so that effects of organic compounds other than PAHs were minimized. The detection limits of the PAHs through the analytical procedure in which the relative standard deviations were less than 15% ranged from 0.4 to 2 ng for different PAH species.

2.4.5. Quality assurance

Analytical methods were checked for the precision and accuracy. All the samples were analyzed in triplicate. Replicate analyses gave an error between ±10% and ±15%. Recoveries ranged from 79% to 95% for the reported PAHs samples. Procedural blanks were performed periodically to prevent contamination. In the present study, all laboratory tools used in sample collection, analysis, and storage were soaked in 10% HNO₃ for two days and then rinsed thoroughly with distilled and double distilled water, respectively, before use.

3. Results and discussion

PAH concentrations in ambient air at the

investigated sites in Shoubra El-Kheima and Helwan areas in Greater Cairo are presented in Table (2). Examined PAHs can be classified according to their number of aromatic ring as follows: 2-ring including NAP; 3-ring including PHE, ACY, ACE, FLU and ANC; 4-ring including FLA, PYR, BaA and CHR; 5-ring including BbF, BkF, BaP and DBA; 6-ring including IND and BgP. Table (2) shows that (The most abundant PAHs were 3-and 5-ring compounds with percentages of 27.8 and 54.2, respectively). Fluctuated concentrations of sixteen PAH species were detected in particulate matter samples in ambient air of Shoubra El-Kheima and Helwan sites. Total content of detected PAHs in ambient air ranged between 141.2 and 888.3 ng/m³ during 2008; and it

ranged between 396.2 and 852.1 during 2009. The highest levels were recorded at Site-4 as illustrated in Fig. 2. Meanwhile, the lowest values were recorded at Site-1. Low level at site-2 could be attributed to low traffic densities/congestion, and absence of big industrial activities compared to other sites of higher PAHs levels.

The highest average concentrations for PAH species in atmosphere of Shoubra El-Kheima and Helwan were BkF of 567.1 ng/m³ followed by DBA with level of 308.2 ng/m³. These results in agreement with the concentrations reported for Cairo atmosphere (Hassan and Khoder, 2011).

Table (2): Atmospheric concentrations (ng/m³) of the individual PAH compounds and different categories of PAHs based on aromatic ring number during the period of study

PAHs		December 2007 to November 2008				December 2008 to November 2009			
		1*	2*	3*	4*	1*	2*	3*	4*
Naphthalene	NAP – 2	14.3	14.2	13.3	14	0.6	0.2	7.7	15.8
Σ2-ring PAHs		14.3	14.2	13.3	14	0.6	0.2	7.7	15.8
Phenanthrene	PHE – 3	21.9	37.2	27.9	41.2	3.5	0.3	10.3	33.4
Acenaphthylene	ACY – 3	14.1 ^b	17.2	21.1	37.3	2.4	3.6	11.5	13.2
Acenaphthene	ACE – 3	10.9	22.7	16.7	30.5	3.8	0.1	4.7	24.6
Fluorene	FLU – 3	24.4	46.5	60.5	54.5	5.4	0.5	15.7	38.5
Anthracene	ANC – 3	34.9	59.3	41.8	60	2	3	18.1	44.2
Σ3-ring PAHs		106.2	182.9	168	223.5	17.1	7.5	60.3	153.9
Fluoranthene	FLA – 4 ^d	21	39.5	18	28.3	1.2	1.3	14.5	26.9
Pyrene	PYR – 4 ^d	15.1	31.1	63.9	44.9	8.3	2.1	12.4	28.3
Benzo(a)anthracene	BaA – 4 ^{ad}	14.6	24.5	26.5	19.8	1	0.9	8	25.5
Chrysene	CRY – 4 ^d	23.1	37.5	47.7	54.1	19.3	30	32.7	45.3
Σ4-ring PAHs		73.8	132.6	156.1	147.1	29.8	34.3	67.6	126
Benzo(b)fluoranthene	BbF – 5 ^{ad}	30.6	33.8	34.1	48.5	15.2	24.2	32.2	41.2
Benzo(k)fluoranthene	BkF – 5 ^d	19.1	32.4	54.5	174.5	95	150.2	128.9	121.7
Benzo(a)pyrene	BaP – 5 ^{ad}	27.3	40.9	79.6	86.1	50.3	64.9	61.8	81.3
Dibenzo(a,h)anthracene	DBA – 5 ^a	25.7	39.8	76.4	96.1	174.3	264.2	231	221.6
Σ5-ring PAHs		102.7	146.9	244.6	405.2	334.8	503.5	453.9	465.8
Indeno(1,2,3-c,d)pyrene	IND – 6 ^{ad}	41.8 ^c	50.1	45.3	55.6	5.1	8.2	30.6	43.6
Benzo(ghi)perylene	BgP – 6 ^d	33.6	36.2	38.5	42.9	8.8	16.3	28.8	47
Σ6-ring PAHs		75.4	86.3	83.8	98.5	13.9	24.5	59.4	90.6
ΣTotal PAHs		372.5	563	665.8	888.3	396.2	570	649	852.1
Total Carcinogenic compounds		98.2	189.1	261.9	306.1	245.9	362.4	363.6	413.2
CPAH (combustible PAHs species)		207.1	293.6	353.4	380.3	109.2	147.9	221.1	339.1

NAP, Naphthalene; PHE, Phenanthrene; ACY, Acenaphthylene; ACE, Acenaphthene; FLU, Fluorine; ANC, Anthracene; FLA, Fluoranthene; PYR, Pyrene; BaA, Benzo(a)anthracene; CRY, Chrysene; BbF, Benzo (b)fluoranthene; BkF, Benzo (k)fluoranthene; BaP, Benzo (a)pyrene; DBA, Dibenzo (a, h)anthracene; IND, Indeno (1,2,3-c,d)pyrene and BgP, Benzo (ghi) perylene.

* Site-1 (North Shoubra El-Kheima), site-2 (South Shoubra El-Kheima), site-3 (North Helwan) and site-4 (South Helwan).

^a Carcinogenic compounds.

^b Maximum concentration carcinogenic contents.

^c Minimum concentration carcinogenic contents.

^d CPAH.

However, total PAHs level in the current study was higher than that reported in previous studies in Egypt. (i.e.) For example (14.79 ng/m^3) in urban area (El-Abasya) in Cairo during the winter season 1997, (7.53 ng/m^3) in summer, (273.8 ng/m^3) in industrial area of Sadat city during 2003 and (29.7 ng/m^3 for indoor and 37.3 ng/m^3 for outdoor) in Cairo (Hassanien, 2001; Ezzo, 2006 and Hassanien, 2006). On individual scale, PAHs ranged between 0.077 ng/m^3 to 308.2 ng/m^3 for (NAP) and (DBA), respectively at Shoubra El-Kheima. Meanwhile it ranged between 0.03 ng/m^3 to 567.1 ng/m^3 for (ACY) and (BkF), respectively at Helwan. Furthermore, Table (2) shows that the highest concentrations of PAH species were recorded at south Shoubra El-Kheima (site-2) and south Helwan (site-4) in similarity to the high atmospheric pollution in these areas due to industrial activities and heavy traffic (EPPP, 2004). PAHs levels in ambient air of the current study were considerably lower than those collected in Greater Cairo ($1,429.74 \text{ ng/m}^3$), in the city center of Cairo ($3,402.8 \text{ ng/m}^3$), in Faysal, Giza ($1,904.2 \text{ ng/m}^3$) and in Taiyuan city (1504.7 ng/m^3) (Peng et al. 2003; Hassan 2006 and Hassan and Khoder, 2011). Meanwhile, it is in agreement with that found by Sharma et al. (2007) in New Delhi, India (891 ng/m^3). In the same way, Smith et al. (1995) demonstrated the contribution of air particulate matter to urban dust reflecting the direct vehicular emissions of PAH and showed a decrease trend in PAH concentrations in atmosphere due to dispersion and deposition.

This is most likely to be due to Cairo climate enhancing the effects of photo-oxidation and volatilization, similar to the finding at Lahore, Pakistan (Smith et al, 1995). Rappaport et al. (2004) found that, NAP (2-ring) represented more than 90% of PAH emissions from creosote facilities and iron foundries and 29% and 16 % of PAH emissions from coke and aluminum production, respectively. The average concentration of particle-bound individual PAHs ranged from 0.4 ng/m^3 for BaP to 9.8 ng/m^3 for FLU in the ambient air of industrial area of Taichung, Taiwan (Fang et al., 2004a). NAP was the most abundant PAH with an average concentration of 330 ng/m^3 at the industrial area in central Taiwan (Fang et al., 2004b). They added that the concentrations were 912 ng/m^3 for total 2- and 3-ring PAHs, 184 ng/m^3 for total 4-ring PAHs, 146 ng/m^3 for total 5-ring PAHs, and 55 ng/m^3 for total 6-ring PAHs. The annual average concentration of PAHs was 114 ng/m^3 at the industrial area of Flanders, Belgium (Ravindra et al., 2006). However, In Hong Kong, the PAHs (4 to 6-rings) levels ranged from 6.46 to 31.7 ng/m^3 at a residential area nearby traffic road, whereas it ranged from 6.52 to 38.8 ng/m^3 at a

residential area near commercial and light industrial area (Sin et al., 2003). They added that, FLA and PYR were the most abundant species at both sites accounting for about 80% of the total PAHs.

Tao et al. (2007) reported that the mean total concentrations of 15 PAHs except NAP of gaseous and particulate phase collected in urban area of Beijing, China were 667 and 331 ng/m^3 in January and 61 and 29 ng/m^3 in March, respectively. On the other hand, Mazquiarán and Pinedo (2007) found that the total PAH levels in Errenteria, Basque Country, Spain were moderate (0.96 – 50 ng/m^3) and showed that a clear seasonal variation with maximum value in winter and minimum value in summer. They found that vehicular traffic was the major source of PAHs in the study area. Meanwhile, Akyüz and Çabuk (2008) reported that the total concentrations of PAHs in particulate matter collected in Zonguldak, Turkey were up to 464.0 ng/m^3 in fine and 28.0 ng/m^3 in coarse fraction in winter, whereas in summer times were up to 22.9 and 3.0 ng/m^3 respectively during the period from January to December in 2007. Higher BaP concentrations were obtained for PM especially in winter. The major pollutant sources for PM were coal combustion and vehicle emissions.

On the other hand, evaporation of PAHs to air from contaminated ground dust may be an important source with an average contribution 68% of total PAHs (Li et al, 2006). Li et al. (2006) suggested in their study that the typical subtropical climate in South China, cool and dry in winter, hot and humid in summer, may control the ambient concentration of PAHs in the air. Also, it has revealed the responsibility effects of temperature, rather than other metrological parameters on PAHs concentrations (Fang et al, 2004). In this concern, prevailing climate of Egypt resembles that of South China, and a similar behave of PAHs in Egyptian environment is expected.

Regarding the obtained concentrations in the current study, levels of BaP were ranged between 27.3 ng/m^3 at north Shoubra El-Kheima (site-1) to 86.1 ng/m^3 at south Helwan (site-4). This range is quiet higher compared to World Health Organization guidelines value 1 ng/m^3 (Fang et al, 2004).

In the present study, the diagnostic ratios of the ambient air PAHs concentrations that characterize the anthropogenic emission at investigated sites during the period of study are shown in table-3. These ratios indicate a greater contribution of the traffic sources to the ambient concentrations of PAHs during the year 2009 more than that the year 2008. This proves the theory of high emission of BgP from traffic sources originated from the main roads (Cairo-Alexandria road for Shoubra El-Kheima sites,

Kornish El-Nile street and Autostrad road for Helwan sites). The diagnostic ratio of IND/BgP was 1.24, 1.39, 1.18 and 1.30 for sites 1, 2, 3 and 4 during the year 2008. While it was 0.58, 0.50, 1.06 and 0.93 during the year 2009. The values of this ratio displayed the similar results, which revealed that they were source of diesel vehicle. This result is in agreement with Sin et al. (2003), who found the ratio of IND/BGP was 0.71 at a residential area near a heavy traffic road. It is also similar to that reported by Hassan (2006) in Greater Cairo.

BGP/IND ratios were 6.53, 4.43, 1.26 and 0.98 for sites 1, 2, 3 and 4 during the year 2008. It was 1.72, 2.0, 0.94 and 1.08 during the year 2009. The values of these ratios displayed high percentage of petrol and diesel engines in all sites. In addition, it indicates a greater contribution of the petrol and

diesel engines sources to the ambient concentrations of PAHs during the year 2008 more than that in the year 2009. This result is in agreement with that found by Rehwagen et al. (2005) at the industrial area (1.16-1.78) and at the urban area (1.71-2.40). It is also similar to that reported by Hassan (2006) in Greater Cairo.

The ratios of IND/(IND+BGP) were 0.55, 0.58, 0.54 and 0.56 for sites 1, 2, 3 and 4 during the year 2008. While it was 0.37, 0.33, 0.52 and 0.48 during the year 2009. It is clear that, the obtained ratios at all investigated sites were similar to that found by Hassan (2006) in Greater Cairo. In addition, it is close to oil combustion for industrial purposes and factories (0.36-0.57) found by Yang et al. (2002); (0.38) found by Fang et al. (2004) and (0.31-0.65) found by Ravindra et al. (2006).

Table (3): Ratios between annual mean concentration of [(BAP/BGP), (IND/BGP), (BGP/IND), (IND/(IND+BGP)) and (BAA/(BAA+CRY)) at investigated sites during the period of study.

Ratio		BaP/BgP	IND/BgP	BgP/IND	IND/(IND+BGP)	BaA/(BaA+CRY)
Dec.2007-Nov.2008						
Shoubra El-Kheima	North (Site-1)	0.81	1.24	6.53	0.55	0.39
	South (Site-2)	1.13	1.39	4.43	0.58	0.40
Helwan	North (Site-3)	2.07	1.18	1.26	0.54	0.36
	South (Site-4)	2.01	1.30	0.98	0.56	0.27
Dec.2008-Nov.2009						
Shoubra El-Kheima	North (Site-1)	5.7	0.58	1.72	0.37	0.05
	South (Site-2)	4.0	0.50	2.00	0.33	0.03
Helwan	North (Site-3)	2.1	1.06	0.94	0.52	0.20
	South (Site-4)	1.7	0.93	1.08	0.48	0.36

The calculated ratios of BaA/(BaA+CRY) were 0.39, 0.40, 0.36 and 0.27 for sites 1, 2, 3 and 4 during the year 2008. While it was 0.05, 0.03, 0.20 and 0.36 during the year 2009. The results were similar to the

value of (0.38-0.64) measured for diesel engines and (0.23-0.89) for industrial areas (Yang et al., 2002; Wu et al., 2005 and Hassan, 2006).

Table (4): The annual mean CPAH, Σ PAH and CPAH / Σ PAH ratio at the investigated sites in Shoubra El-Kheima and Helwan.

Site		Dec.2007-Nov.2008		
		CPAH (ng/m ³)	Σ PA H (ng/m ³)	CPAH / Σ PAH
Shoubra El-Kheima	North (Site-1)	207.1	372.5	0.56
	South (Site-2)	293.6	563.0	0.52
Helwan	North (Site-3)	353.4	665.8	0.53
	South (Site-4)	380.3	888.3	0.43
Site		Dec.2008-Nov.2009		
		CPAH (ng/m ³)	Σ PA H (ng/m ³)	CPAH / Σ PAH
Shoubra El-Kheima	North (Site-1)	109.2	396.2	0.28
	South (Site-2)	147.9	570.0	0.26
Helwan	North (Site-3)	221.1	649.0	0.34
	South (Site-4)	339.1	852.1	0.40

Typical combustion origin PAHs can be indicated by CPAH (combustible PAHs species; FLA, PYR, BaA, CRY, BbF, BkF and BbP). In the present study, the annual mean CPAH/ Σ PAH ratio at the four investigated sites is shown in Table (4). The annual mean CPAH/ Σ PAH ratios were 0.56, 0.52, 0.53 and 0.43 for sites 1, 2, 3 and 4 for the year 2008. While it were 0.28, 0.26, 0.34 and 0.40 for the year 2009. These ratios were similar to that found for non-catalyst equipped automobiles and heavy-duty diesel trucks. These results are in agreement with Hassan (2006) in Cairo, Bi et al. (2003) in Guangzhou, China (0.31-0.46). In the present study, the mean CPAH/ Σ PAH ratio indicates that combustion, rather than unburned fossil fuels in power plants, is the principle source of the observed PAH.

BaP is one of the most important PAHs because of its carcinogenic properties. It has been regarded as the compound with the most important consequences for human health because it is a potent PAH carcinogen classified in group-2A (IARC, 1983 and WHO, 1987). It considered a sufficient index for PAH carcinogenicity.

In the present study, the annual mean concentrations of BaP were 27.3, 40.9, 79.6 and 86.1 for sites-1 (north Shoubra El-Kheima), site-2 (south Shoubra El-Kheima), site-3 (north Helwan) and site-4 (south Helwan) for the year 2008. While it was 50.3, 64.9, 61.8 and 81.3 for the year 2009 (as shown in Tables-1). It is clear that, the highest annual average concentration of BaP was recorded at south Helwan (site-4) during the years 2008 and 2009, whereas the lowest annual average was recorded at north Shoubra El-Kheima (site-1) during the year 2008. World Health Organization set up a guidelines value 1 ng/m^3 (Fang et al. (2004).

The carcinogenicity classifications verified by EPA Carcinogenicity Risk Assessment Endeavor Work Group (USEPA, 1995) showed that BaA, BbF, BaP, DBA and IND are considered to be probable human carcinogens, whereas other PAHs such as ACY, ANC, BgP, FLA, PYR and FLU are not classified as promoters of the same health risk (IARC,1983). In the current study, the seasonal and annual percentage of the total carcinogenic compounds (BaA, BbF, BaP, DBA and IND) to the Σ PAH16 for sites 1, 2, 3 and 4 are shown in Fig. 2. From these figure, it is clear that, the percentages of the total carcinogenic compounds are differ from one site to other. Where, it is higher during the year of 2009 than that in the year of 2008. This may be due to the increase of automobiles emission beside the industrial particles.

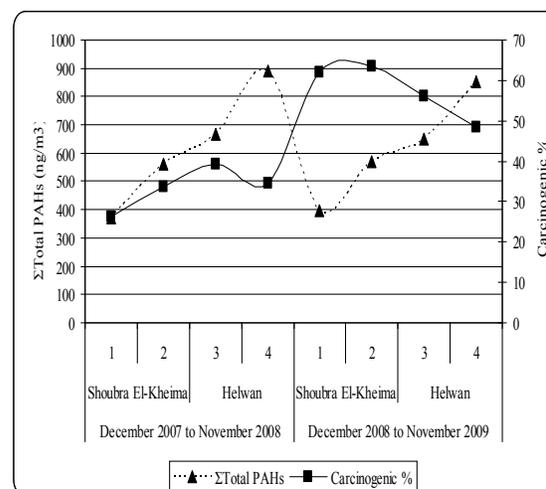


Figure (2): Total concentrations of PAH and carcinogenic percent at investigated sites in Shoubra El-Kheima during study period.

4. Conclusions

This work revealed the level of PAHs in ambient air of Shoubra El-Kheima and Helwan areas of Greater Cairo. It extends our understanding of the current PAHs contamination status in this mega city. The average concentration of 16 PAHs was 475.4 ng/m^3 at Shoubra El-Kheima and 619.6 ng/m^3 at Helwan with carcinogenic content of 46.4% of total PAHs at Shoubra El-Kheima and 44.6% at Helwan. The present study confirms the contribution of vehicular traffic, industrial emissions, power plant emission and the incomplete combustion of open waste burning to atmospheric PAHs. This study suggested that the pollution of PAHs in Shoubra El-Kheima and Helwan should emphasize on controlling the industrial and power plants emissions and traffic exhausts. Further work is required to develop this preliminary investigation, including many more measurements in locations representing other activities. It is also realized that typical environment in Egypt of high temperature and relative humidity, coupled with abundant sunshine, may differ the chemistry of PAHs from that of other geographical regions.

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