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Seasonal Variation of Volatile Poly Aromatic Hydrocarbons (PAHs) Released from Different Sources in South Cairo

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Abstract

Based on a year-round data-set (from January to November 2014), an intensive air sampling program was conducted during 2014 in four different function sites in South El-Tabbin city to study the temporally and spatially characteristics of Poly Aromatic Hydrocarbons (PAHs) in the gaseous and particulate phases. This area is considered as one of the most polluted areas in Egypt as it includes heavy industrial plants, as well as it is bounded by heavy traffic. A total of 48 atmospheric samples were collected by a high-volume active air sampler. The gaseous and particulate phases of PAHs were extracted and analyzed using Gas chromatography/mass spectrometry together. The total concentrations of the sixteen PAHs (which tagged the United States Environmental Protection Agency priority) in the air of the study area ranged from 76.48 ± 19.44 µg/m^3 to 26995.86 ± 2835.91 µg/m^3. The average PAHs concentration in the coke production site was ~ 355 times of that in the residential area site. For the whole study area; 4, 5, and 6 rings PAHs were dominant and accounting for ~66% – ~84%. The total concentrations of combustion derived PAHs were ranged from 63.24 ± 17.35 µg/m^3 to 17546.97 ± 1848.55 µg/m^3 covering 65% − 83% of total PAHs which indicating large amounts of combustion sources existed from them in South El-Tabbin city. Seasonal trends of PAHs concentrations were observed with a high concentration in winter and low in summer where the average concentration of PAHs in winter was ~1.6 times higher than that in summer.

Keywords: Air Pollution, Poly Aromatic Hydrocarbons (PAHs), Combustion derived Polycyclic Aromatic Hydrocarbons (COMPAHs), Gas chromatography mass spectrometry (GC/MS), El-Tabbin City

1. Introduction

Air with high concentrations of PAHs causes many adverse effects on different types of organisms, including plants, birds, and mammals. Some studies reported that there is a significant positive correlation between mortality by lung cancer in humans and exposure to PAHs from the exhaust from coke ovens, roofing-tar, and cigarette smoke. Some PAHs have been demonstrated to be carcinogenic in humans and experimental animals, and they are classified as carcinogenic materials by many organizations, including the United States Agency for Toxic Substances and Disease Registry (US ATSDR), the International Agency for Research on Cancer (IARC), the Department of Health and Human Services (DHHS), the National Occupation Safety and Health Administration (OSHA), and the USEPA. Light Molecular Weight (LMW) PAHs, except naphthalene, usually are associated with relatively lower toxicity (cancer risk) than Light Molecular Weight (HMW) PAHs with 5 or 6 aromatic rings. In other words, as molecular weight increases, the carcinogenicity of PAHs also increases with reducing acute toxicity. However, the most potent PAHs carcinogens have been identified to include anthracene (ANT), benzo[a]anthracene (BaA), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DBahA), chrysene (CHR), fluorine (FLO), and pyrene (PYR) (Armstrong et al., 2004; Bach et al., 2003; Public Health England, 2018; Canadian Council of Ministers of the Environment (CCME), 2010; Delgado-Saborit et al., 2011; Environmental Programs Directorate, 2011).

There is much information on the multi-ringed heavier PAHs but have left the lighter vapor-phase PAH components rather neglected. Although these lighter compounds have weaker carcinogenic/mutagenic properties, they are the most abundant in the urban atmosphere and react with other pollutants to form more toxic derivatives (Park et al., 2002). Thus, the implication of human exposure to mixtures of PAHs, rather than to individual substances, is important. The levels of individual PAHs vary over several orders of magnitude and are generally in the range of several ng/m3 to several µg/m3, which making an assessment on a regional scale difficult (Pandit et al., 2006; Singh et al., 2011).

The main objectives of this work can be summarized in the following points; 1) Measuring the concentration levels of ambient PAHs in gaseous and particulate phases, 2) Study the spatial and temporal variations of ambient PAH levels and their possible relationships with meteorological parameters, and 3) Identify and allocate possible sources of PAHs using diagnostic ratio. Results of this work obtained from an approximately 1-year sampling/analysis campaign of particulate and gaseous PAHs in different seasons during 2014 at four different sites in the city of El-Tabbin which considered one of the most polluted areas in Egypt.

2. Methodology and Techniques

2.1 Description of the Study Area

The study area for this study is located in the south of El-Tabbin city, as shown in Figure 1, with geographical coordinates of 29 °44'59.92" N to 29 °47'35.12" N latitude and 31 °17'35.45"

E to 31 °20'12.13" E longitude, and a total area of 25 km2. The selected sampling area is surrounded by a mixture of urban, industrial, commercial and traffic activities as they are possible sources of PAHs especially the coke production plant. Furthermore, this area represents a large urban industrialized area in El-Tabbin city and even in Helwan city where metallurgical, chemical, coal, petrochemical, bricks and cement-producing plants are located. Acronyms, coordinates, and activities of sampling sites are indicated in Table 1. Distances between these sites are indicated in Figure 2.

Table 1. Sampling sites acronyms, coordinates, and activities

Site Location	Acronyms	Latitude (N)	Longitude (E)	Site Activity Description
Tabbin Institute	TIMS	29 °46'54.57"	31 °18'47.45"	Traffic and Industrial area
Residential Area	RA	29 °46'37.85"	31 °17'41.11"	Residential and Traffic area
Coke Factory	CK	29 °45'54.70"	31 °18'52.44"	Industrial area
Arab Abu Said	AAS	29 °45'46.62"	31 °21'36.93"	Traffic and Industrial area

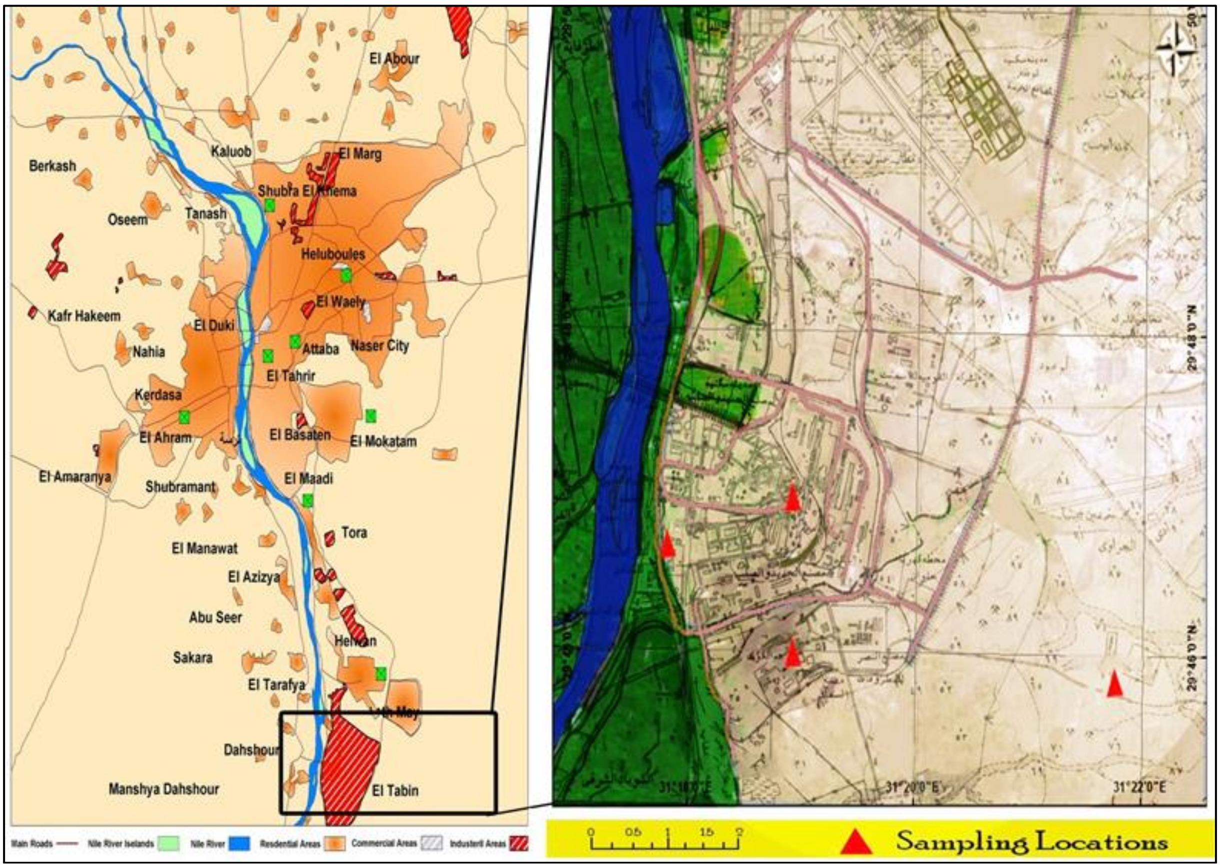

Figure 1. Map for Greater Cairo and study area with sampling locations

Figure 2. Sampling sites on Google Earth map

2.2 Applied Methodology

The applied methodology in this study is originated from the US EPA Method TO-13A (Compendium Method for determination of PAHs in ambient air), (US EPA, 1999). Concisely, the method is based on using a High-Volume Air Sampler (Andersen Instruments Inc., 500 Technology Ct., Smyrna, GA) for the collection of PAHs from ambient air onto the sampling module that consists of particle filter and high-volume collection tube containing adsorbent media (i.e. sorbent cartridge). This system is capable of pulling ambient air through the filter/sorbent cartridge at a flow rate of approximately 225 l/min (i.e. 0.225 m^3/min) to obtain a total sample volume of greater than 300 m^3 over a 24-hour period. Moreover, this method provides an efficient collection of most PAHs involving two-member rings or higher either in a particulate phase or in a gaseous phase through the utilization of quartz fiber filter with adsorbent cartridge consists of both polyurethane foam (PUF) and XAD-2® resin as a sorbent media where XAD-2® is intermediated between two layers of PUF in sandwiching configuration in order to minimize breakthrough of highly volatile PAHs. The sampling module inside the high-volume sampler is consists of metal filter holder capable of holding a 102-mm circular particle filter supported by a 16-mesh stainless-steel screen and attaching to a metal cylinder capable of holding a 65-mm outer diameter (OD) and 60-mm inner diameter (ID) x 125-mm in height borosilicate glass sorbent cartridge containing the adsorbent media (PUF and XAD-2®). The Gas Chromatography/Mass Spectroscopy (GC/MS) instrument is combined of two parts: GC that separates the chemicals in the sample and MS that identifies and quantifies the chemicals., for general specifications for Shimadzu - GCMS-QP5050A, it is a benchtop quadrupole mass spectrometer features an extended mass range to 900 Daltons and optional positive and negative chemical ionization (PCI and NCI). This wide variety of ionization modes and the ability to analyze high molecular weight compounds make the GCMS-QP5050A the answer to different application requirements. Furthermore, The

GCMS-QP5050A can detect 100 pg of methyl stearate at S/N better than 60 in scan mode 'Single (or Selected) Ion Monitoring (SIM) mode is even more sensitive'. Scan speeds of up to 6,750 AMU/sec. are achieved with unit mass resolution. The MS is paired with GC-17A gas chromatograph, which uses Advanced Flow Control (AFC) for rapid, reproducible results. Additionally, all ion source parts can be accessed from the front of the instrument for easy maintenance. The efficient 150 L/sec turbomolecular pump and rotary pump quickly achieve a high vacuum in less than 5 minutes and this will reflect in minimal downtime. For developing calibration curve for GC/MS analysis, the stock standard solution of 16 PAHs mixed in methylene chloride: methanol (50:50) at the concentration of 2000 µg/ml (Sigma Aldrich Chemical Co. Inc. USA) was diluted first to the concentration of 25 ng/µL by taking 125 µL of the stock PAH standard and diluting with hexane in a 10-mL volumetric flask. After that, five concentration levels of PAH standards (i.e., 2.50 ng/µL, 1.25 ng/µL, 0.50 ng/µL, 0.25 ng/µL, and 0.10 ng/µL) were prepared prior GC/MS analysis, each 1 mL aliquot of the five calibration standards as well as 1mL portion of the sample extracts are spiked with 10 µL at concentration of 50 ng/ µL (after 1:40 dilution) of the mixture of deuterated PAH internal standard (Isotopically labeled PAH isomers at the concentration of 2000 µg/mL mixed in methylene chloride, Sigma Aldrich Chemical Co. Inc. USA), to yield a final concentration of 0.5 ng. This internal standard was used to quantify and correct the amounts of specific PAHs found in the samples.

2.3 Identification and Quantification of PAHs

Identification of PAHs compounds was based on comparing the measured mass spectra and retention times to reference standards. It was calculated by using eq. 1.

$$\boldsymbol{Concentration, (ng/std\, m^3)} = \frac{\boldsymbol{A_x I_s V_t D_f}}{\boldsymbol{A_{is} V_i \overline{RRF}}} \tag{1}$$

Where,

A_x = area response for the compound to be measured, counts

A_{is} = area response for the internal standard, counts.

I_s = amount of internal standard, ng/µL.

RRF_i = the mean RRF from the most recent initial calibration, dimensionless.

V_i = volume of air sampled, std m^3.

V_t = volume of final extract, µL.

D_f = dilution factor for the extract. If there was no dilution, D_f equals 1. If the sample was diluted, the D_f is greater than 1.

3. Results and Discussion

In this study 16 PAHs were analyzed including includes Naphthalene (NAP), Acenaphthene (ACE), Acenaphthylene (ACY), Fluorene (FLO), Phenanthrene (PHE), Anthracene (ANT), Fluoranthene (FLA), Pyrene (PYR), Benz[a]Anthracene (BaA), Chrysene (CHR), Benzo[b]Fluoranthene (BbF), Benzo[k]Fluoranthene (BkF), Benzo[a]Pyrene (BaP), Dibenz[ah]Anthracene (DBahA), Indeno[l,2,3-cd]Pyrene (IcdP) and Benzo[ghi]Perylene (BghiP). Indubitably, the environmental locations of the sampling sites are considered as an important contributor to the concentrations of atmospheric PAHs. Because the sources of PAHs are almost related to combustion, the specific local sources may lead to the differences in PAH concentrations for different sites in a city or area under study. Therefore, the comparison studies of atmospheric PAHs in different functional zones are necessary for establishing effective controlling measures in an urban area. Furthermore, owing to the difference in population, traffic density, and industry distribution, the PAH contribution from anthropogenic inputs varied in different function zones (Lodovici et al., 2003, Kong et al., 2010, Kim et al., 2013).

The summary of the atmospheric PAHs mass concentrations for different sampling sites and seasons under study are provided in Tables (2): (5). As can be seen, the total amounts of analyzed PAHs (i.e. Total ∑16 PAHs) in the area under study varied from 76.48 ± 19.44 µg/m^3 in RA site to 26995.86 ± 2835.91 µg/m^3 in the CK site with a mean concentration of 7085.08 ± 773.98 µg/m^3. PAHs concentrations demonstrate that the area under study is influenced by regional sources. In the nutshell, the total ∑16 PAHs concentrations, as well as the average concentrations of ∑16 PAHs over the seasonal sampling period in the different functional zones of the study area can be ordered as follow: CK site (at the border of Coke production plant) (26995.86 ± 2835.91 µg/m^3 with the average concentration of 6749 ± 709 µg/m^3) > TIMS site (at the prevailing wind directions carried the combustion emissions coming from stationary sources of several industrial complexes) (901.34 ± 166.22 µg/m^3 with the average concentration of 225 ± 42 µg/m^3) > AAS site (at ≤ 1 Km northwest of the stationary exhausts of the bricks plants) (366.64 ± 74.35 µg/m^3 with the average concentration of 92 ± 17 µg/m^3) > RA site (dual impacts from the vicinity to industrial complexes and vehicle emissions) (76.48 ± 19.44 µg/m^3 with the average concentration of 19 ± 4 µg/m^3).

In comparing to others, Wu et al. (2014) pointed out that the total PAHs concentrations associated with $PM_{2.5}$ and PM_{10} in the E'erduosi city in china decreasing as coal-chemical base site > heavy industrial site > residential site with heavy traffic > suburban site surrounded by grassland > background site where PAHs concentrations in the coal-chemical base site are 250 and 31 times of those in the background site for $PM_{2.5}$ and PM_{10}, respectively.

On the other hand, Kong et al. (2010) concluded that PAHs concentrations associated with $PM_{2.5}$ in ten sites in five cities covering different city zones of Liaoning Province exhibit the following order as residential/commercial site (1900.89 ng/m^3) > commercial site (1053.83 ng/m^3) > industrial/commercial site (923.01 ng/m^3) > residential site (300.41 ng/m3) > urban background site (227.01 ng/m^3) > industrial site (75.32 ng/m^3). It should be noted that the industrial site is located in a coastal city where the air quality is well than the other four cities.

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Table 2. Average of the PAHs mass concentrations (μg/m^3) found in the Coke site over the seasonal sampling period

PAHs	**Winter**	**Spring**	**Summer**	**Fall**	**$\sum_i$ PAH[b]**
NAP	**1872.64 ±370.06[a]**	**1209.88 ±95.55**	**771.68 ±42.05**	**1281.14 ±164.08**	**5135.34 ±671.74**
ACE	**135.82 ±12.23**	**123.98 ±7.48**	**105.07 ±20.93**	**114.53 ±4.41**	**479.40 ±45.03**
ACY	**9.85 ±0.93**	**8.65 ±0.16**	**6.50 ±0.72**	**8.13 ±0.36**	**33.13 ±2.17**
FLO	**77.93 ±8.26**	**64.18 ±5.09**	**58.93 ±4.30**	**82.96 ±7.52**	**284.01 ±25.13**
PHE	**823.67 ±14.88**	**666.35 ±29.99**	**590.27 ±48.30**	**699.07 ±74.55**	**2779.35 ±167.72**
ANT	**151.08 ±6.81**	**132.65 ±6.32**	**149.40 ±13.22**	**150.18 ±21.25**	**583.31 ±47.61**
FLA	**1101.35 ±62.46**	**1017.33 ±30.00**	**853.84 ±66.15**	**993.31 ±50.56**	**3965.83 ±209.18**
PYR	**861.64 ±67.52**	**770.17 ±34.90**	**747.33 ±32.33**	**807.57 ±113.34**	**3186.71 ±248.10**
BaA	**285.67 ±36.61**	**260.31 ±22.33**	**221.24 ±29.41**	**257.36 ±29.82**	**1024.57 ±118.12**
CHR	**348.43 ±22.68**	**311.18 ±29.48**	**276.03 ±21.16**	**296.98 ±60.21**	**1232.62 ±133.54**
BbF	**815.67 ±34.15**	**640.00 ±93.58**	**523.33 ±107.34**	**745.33 ±59.97**	**2724.33 ±295.04**
BkF	**370.57 ±57.44**	**264.00 ±44.51**	**200.33 ±46.14**	**336.67 ±66.15**	**1171.57 ±214.25**
BaP	**540.00 ±102.56**	**413.33 ±86.69**	**312.00 ±22.34**	**391.37 ±40.81**	**1657.00 ±252.39**
IcdP	**401.00 ±58.92**	**324.67 ±64.49**	**230.00 ±35.59**	**292.52 ±79.10**	**1248.33 ±238.11**
DBahA	**43.41 ±10.10**	**39.72 ±6.26**	**30.36 ±4.35**	**40.87 ±7.20**	**154.35 ±27.91**
BghiP	**426.00 ±21.79**	**333.00 ±43.97**	**258.67 ±40.07**	**318.33 ±34.03**	**1336.00 ±139.86**
$\sum_{16}$ PAHs[c]	**8264.74 ±887.42**	**6579.40 ±600.78**	**5334.98 ±534.33**	**6816.75 ±813.37**	
LMW-PAHs[d]	**3071.00 ±413.18**	**2205.68 ±144.59**	**1681.85 ±129.52**	**2336.01 ±272.16**	
MMW-PAHs[e]	**2597.09 ±189.27**	**2359.00 ±116.71**	**2098.44 ±148.97**	**2355.21 ±253.94**	
HMW-PAHs[f]	**2596.65 ±284.97**	**2014.72 ±339.48**	**1554.69 ±255.84**	**2125.53 ±287.27**	
∑ C-PAHs[g]	**2804.75 ±322.47**	**2253.21 ±347.32**	**1793.29 ±266.26**	**2361.53 ±343.27**	
∑ COM-PAHs[h]	**5150.33 ±464.15**	**4334.00 ±449.93**	**3622.77 ±400.46**	**4439.87 ±534.01**	
Total $\sum_{16}$ PAHs[i]	**26995.86 ±2835.91**				

[a] Mean value (from 3 consecutive sampling weeks) ±Standard deviation.

[b] ∑i PAH: Summation of the individual PAH concentrations over the seasonal sampling period.

[c] ∑16 PAHS: Summation of 16 PAHs concentrations for each sampling season.

[d] LMW-PAHs: Total Low Molecular PAHs (including NAP, ACE, ACY, FLO, PHE, and ANT) for each sampling season.

[e] MMW-PAHs: Total Low Molecular PAHs (including FLA, PYR, BaA, and CHR) for each sampling season.

[f] HMW-PAHs: Total Low Molecular PAHs (including BbF, BkF, BaP, IcdP, DBahA, and BghiP) for each sampling season. g ∑ C-PAHs: Total carcinogenic PAHs (including BaA, CHR, BbF, BkF, BaP, IcdP, and DBahA) for each sampling season.

[h] ∑ COM-PAHs: Total combustion derived PAHs (including FLA, PYR, CHR, BbF, BkF, BaA, BaP, IcdP, and BghiP) for each sampling season.

[i] Total ∑16 PAHs: Total summation of 16 PAHs concentrations over the seasonal sampling period at the specific sampling site.

Table 3. Average of the PAHs mass concentrations (µg/m^3) found in the Tabbin Institute site over the seasonal sampling period

PAHs	Winter	Spring	Summer	Fall	∑i PAH
NAP	**33.10 ±5.56**	**22.10 ±3.57**	**17.00 ±2.91**	**27.57 ±3.58**	**99.77 ±15.62**
ACE	**3.17 ±0.30**	**2.01 ±0.32**	**1.39 ±0.37**	**2.51 ±0.57**	**9.07 ±1.55**
ACY	**2.07 ±0.40**	**1.26 ±0.26**	**0.91 ±0.07**	**1.76 ±0.26**	**6.00 ±0.98**
FLO	**9.64 ±2.15**	**6.84 ±1.12**	**5.45 ±0.68**	**7.60 ±1.86**	**29.53 ±5.81**
PHE	**51.32 ±6.29**	**38.91 ±3.93**	**29.80 ±4.43**	**44.80 ±7.00**	**164.82 ±21.64**
ANT	**10.03 ±3.47**	**7.75 ±3.12**	**5.46 ±2.25**	**7.07 ±2.53**	**30.31 ±11.37**
FLA	**33.89 ±6.38**	**25.96 ±5.62**	**16.19 ±4.05**	**27.90 ±2.81**	**103.95 ±18.87**
PYR	**28.26 ±3.81**	**20.01 ±2.21**	**13.58 ±4.76**	**24.41 ±3.40**	**86.25 ±14.18**
BaA	**24.78 ±4.26**	**19.09 ±4.47**	**13.43 ±3.25**	**24.92 ±3.90**	**82.22 ±15.88**
CHR	**27.61 ±4.44**	**22.27 ±4.07**	**16.44 ±5.69**	**26.47 ±4.16**	**92.80 ±18.36**
BbF	**7.66 ±0.90**	**5.87 ±0.89**	**4.13 ±0.66**	**6.73 ±1.29**	**24.38 ±3.73**
BkF	**18.86 ±1.81**	**14.50 ±2.39**	**9.04 ±1.84**	**14.60 ±2.45**	**57.00 ±8.49**
BaP	**11.35 ±1.64**	**8.59 ±1.85**	**5.49 ±1.57**	**8.22 ±1.88**	**33.65 ±6.93**
IcdP	**10.95 ±3.07**	**7.96 ±3.18**	**5.49 ±2.35**	**8.02 ±2.38**	**32.42 ±10.98**
DBahA	**4.52 ±0.63**	**3.44 ±0.33**	**2.14 ±0.25**	**3.18 ±0.49**	**13.28 ±1.69**
BghiP	**12.16 ±3.14**	**9.33 ±2.75**	**5.83 ±1.91**	**8.57 ±2.32**	**35.89 ±10.12**
∑16 PAHs	**289.36 ±48.24**	**215.90 ±40.06**	**151.75 ±37.04**	**244.32 ±40.87**	
LMW-PAHs	**109.32 ±18.17**	**78.87 ±12.31**	**60.00 ±10.70**	**91.30 ±15.80**	
MMW-PAHs	**114.54 ±18.89**	**87.34 ±16.39**	**59.64 ±17.75**	**103.70 ±14.27**	
HMW-PAHs	**65.50 ±11.19**	**49.70 ±11.37**	**32.11 ±8.58**	**49.32 ±10.80**	
∑ C-PAHs	**105.73 ±16.75**	**81.73 ±17.17**	**56.16 ±15.61**	**92.14 ±16.54**	
∑ COM-PAHs	**175.52 ±29.45**	**133.59 ±27.43**	**89.61 ±26.09**	**149.84 ±24.59**	
Total ∑16 PAHs	**901.34 ±166.22**				

Table 4. Average of the PAHs mass concentrations (µg/m^3) found in the Arab Abu Said site over the seasonal sampling period

PAHs	**Winter**	**Spring**	**Summer**	**Fall**	**∑i PAH**
NAP	**0.65 ±0.14**	**0.42 ±0.05**	**0.27 ±0.02**	**0.44 ±0.07**	**1.78 ±0.28**
ACE	**1.97 ±0.12**	**1.80 ±0.16**	**1.52 ±0.27**	**1.66 ±0.04**	**6.95 ±0.60**
ACY	**0.14 ±0.02**	**0.13 ±0.01**	**0.09 ±0.01**	**0.12 ±0.01**	**0.48 ±0.04**
FLO	**1.13 ±0.09**	**0.93 ±0.07**	**0.86 ±0.08**	**1.20 ±0.12**	**4.12 ±0.36**
PHE	**18.29 ±1.78**	**13.95 ±4.48**	**14.81 ±3.73**	**19.43 ±2.33**	**66.48 ±12.32**
ANT	**2.25 ±0.10**	**1.98 ±0.09**	**2.23 ±0.20**	**2.24 ±0.32**	**8.71 ±0.73**
FLA	**15.99 ±1.34**	**14.74 ±0.15**	**12.37 ±0.69**	**14.41 ±1.0**	**57.51 ±3.12**
PYR	**14.85 ±5.36**	**13.18 ±3.44**	**11.50 ±3.70**	**12.74 ±2.43**	**52.27 ±14.00**
BaA	**5.15 ±2.26**	**4.45 ±1.22**	**3.88 ±1.67**	**4.40 ±0.77**	**17.88 ±5.34**
CHR	**5.06 ±0.45**	**4.18 ±1.00**	**4.00 ±0.34**	**4.31 ±0.89**	**17.54 ±2.65**
BbF	**11.84 ±0.84**	**9.31 ±1.63**	**7.57 ±1.39**	**10.80 ±0.58**	**39.52 ±4.73**
BkF	**5.40 ±1.00**	**3.84 ±0.76**	**2.92 ±0.75**	**4.90 ±1.07**	**17.04 ±3.51**
BaP	**7.86 ±1.69**	**6.02 ±1.44**	**4.53 ±0.43**	**5.69 ±0.75**	**24.09 ±4.31**
IcdP	**5.83 ±1.02**	**4.73 ±1.06**	**3.33 ±0.56**	**4.27 ±1.27**	**18.15 ±3.81**
DBahA	**0.63 ±0.16**	**0.58 ±0.11**	**0.44 ±0.07**	**0.59 ±0.12**	**2.25 ±0.46**
BghiP	**10.18 ±5.70**	**8.17 ±5.35**	**6.25 ±2.20**	**7.27 ±3.19**	**31.88 ±14.44**
∑16 PAHs	**107.21 ±22.07**	**88.39 ±21.01**	**76.56 ±16.02**	**94.49 ±15.26**	
LMW-PAHs	**24.43 ±2.25**	**19.20 ±4.86**	**19.78 ±4.30**	**25.10 ±2.90**	
MMW-PAHs	**41.04 ±9.41**	**36.55 ±5.81**	**31.75 ±6.40**	**35.86 ±5.08**	
HMW-PAHs	**41.73 ±10.40**	**32.64 ±10.34**	**25.03 ±5.31**	**33.53 ±7.28**	
∑ C-PAHs	**41.76 ±7.41**	**33.09 ±7.21**	**26.67 ±5.11**	**34.96 ±5.74**	
∑ COM-PAHs	**82.14 ±19.65**	**68.61 ±16.04**	**56.34 ±11.64**	**68.79 ±12.24**	
Total ∑16 PAHs	**366.64 ±74.35**				

Table 5. Average of the PAHs mass concentrations (μg/m^3) found in the Residential Area site over the seasonal sampling period

PAHs	Winter	Spring	Summer	Fall	∑i PAH
NAP	**0.15 ±0.04**	**0.10 ±0.02**	**0.06 ±0.01**	**0.10 ±0.02**	**0.42 ±0.08**
ACE	**0.46 ±0.01**	**0.42 ±0.06**	**0.36 ±0.05**	**0.39 ±0.03**	**1.63 ±0.16**
ACY	**0.34 ±0.03**	**0.05 ±0.01**	**0.03 ±0.01**	**0.12 ±0.01**	**0.54 ±0.02**
FLO	**0.26 ±0.02**	**0.22 ±0.02**	**0.20 ±0.03**	**0.28 ±0.04**	**0.97 ±0.07**
PHE	**1.98 ±0.29**	**1.65 ±0.33**	**1.76 ±0.21**	**1.71 ±0.50**	**7.10 ±1.34**
ANT	**0.53 ±0.03**	**0.47 ±0.05**	**0.53 ±0.08**	**0.53 ±0.09**	**2.05 ±0.25**
FLA	**3.10 ±0.76**	**2.96 ±0.30**	**2.57 ±0.54**	**2.92 ±0.32**	**11.56 ±1.97**
PYR	**3.53 ±1.40**	**3.13 ±0.50**	**2.73 ±1.02**	**3.01 ±0.75**	**12.40 ±4.26**
BaA	**1.40 ±0.32**	**1.11 ±0.32**	**0.93 ±0.43**	**1.03 ±0.19**	**4.47 ±1.36**
CHR	**1.19 ±0.16**	**0.98 ±0.24**	**0.85 ±0.05**	**0.87 ±0.15**	**3.89 ±0.63**
BbF	**2.79 ±0.37**	**2.20 ±0.52**	**1.77 ±0.28**	**2.54 ±0.29**	**9.30 ±1.46**
BkF	**1.28 ±0.23**	**0.91 ±0.23**	**0.69 ±0.12**	**1.16 ±0.32**	**4.04 ±1.08**
BaP	**1.86 ±0.50**	**1.43 ±0.34**	**1.07 ±0.17**	**1.34 ±0.25**	**5.70 ±1.35**
IcdP	**1.38 ±0.32**	**1.12 ±0.31**	**0.78 ±0.10**	**1.01 ±0.36**	**4.29 ±1.10**
DBahA	**0.15 ±0.04**	**0.14 ±0.03**	**0.10 ±0.02**	**0.14 ±0.04**	**0.53 ±0.14**
BghiP	**2.45 ±1.51**	**1.92 ±1.24**	**1.48 ±0.55**	**1.74 ±0.85**	**7.58 ±4.15**
∑16 PAHs	**22.85 ±6.25**	**18.81 ±5.13**	**15.90 ±3.84**	**18.82 ±4.22**	
LMW-PAHs	**3.73 ±0.39**	**2.91 ±0.49**	**2.94 ± 0.38**	**3.13 ±0.69**	
MMW-PAHs	**9.22 ±2.81**	**8.19 ±1.88**	**7.07 ± 2.11**	**7.84 ±1.42**	
HMW-PAHs	**9.90 ±3.05**	**7.71 ±2.76**	**5.90 ±1.34**	**7.94 ±2.11**	
∑ C-PAHs	**10.04 ±2.11**	**7.89 ±2.10**	**6.19 ± 1.30**	**8.10 ± 1.60**	
∑ COM-PAHs	**18.97 ±5.81**	**15.77 ±4.61**	**12.87 ±3.44**	**15.64 ±3.49**	
Total ∑16 PAHs	**76.48 ±19.44**				

For the sake of illustration, Figure 3 shows the measured total PAH concentrations (i.e. Total ∑16 PAHs) over the seasonal sampling period for the different sampling sites, while Figure 4 shows the measured total PAHs concentrations for each compound (∑i PAHs) over the seasonal sampling period for each sampling site. Obviously from both figures, the highest mass concentrations of PAHs among the four sampling sites (either for Total ∑16 PAHs or ∑i PAHs) are found in the Coke samples whereas the lowest values are found in the Residential Area samples.

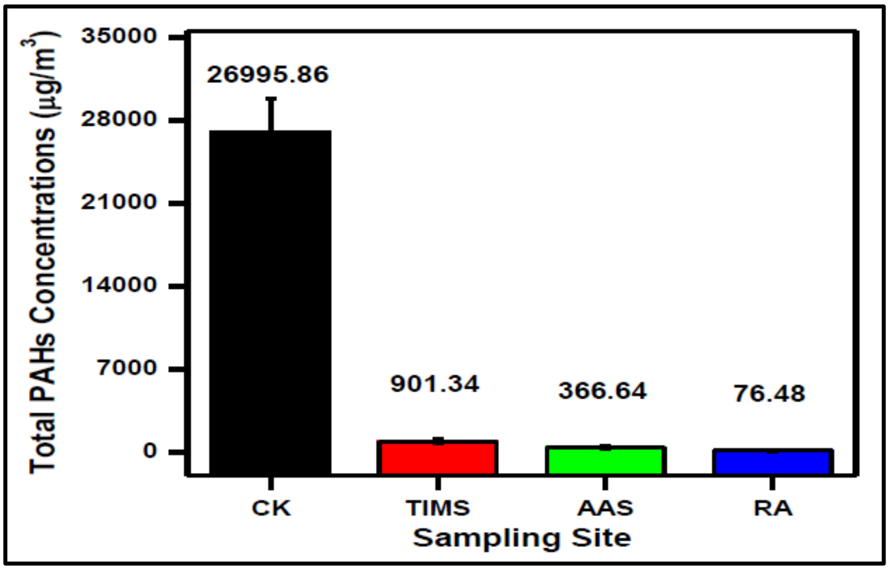

Figure 3. Total PAHs Concentrations over the seasonal sampling period for the sampling sites

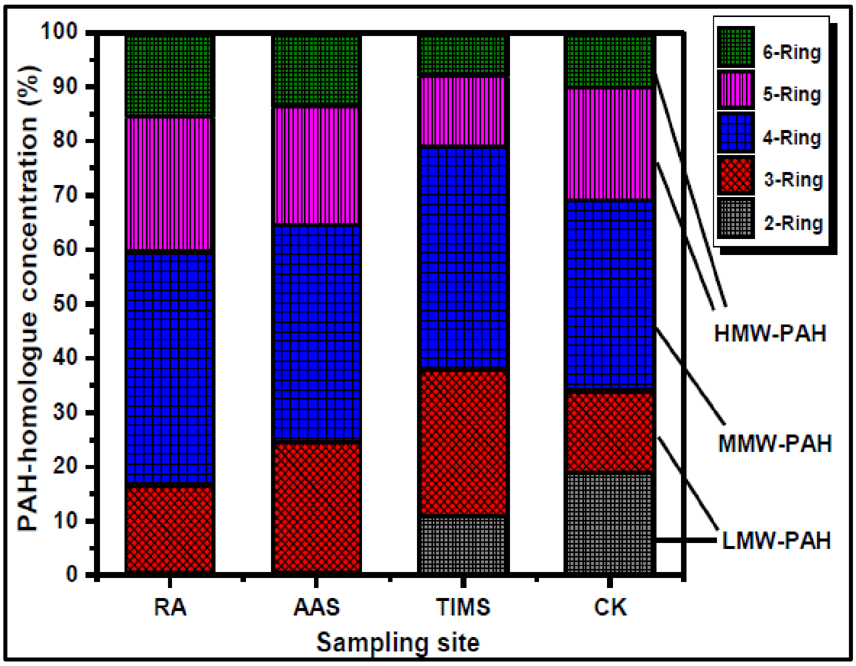

Figure 4. PAH-Homologue concentrations of samples from different sampling sites

Kim et al. (2013) also indicated that the highest values for atmospheric PAHs are generally found when industrial, rather than traffic or residential, contributions are dominant. On the other hand, Zhang and Tao (2009) concluded that biofuel; wildfire, domestic coal combustion, coke production, and open straw burning are the most important sources for global atmospheric PAHs, accounting for 56.7%, 12.4%, 11.7%, 7.0%, and 2.7%, respectively. However, the combustion derived PAHs (COMPAHs), including FLA, PYR, CHR, BbF, BkF, BaA, BaP, IcdP, BghiP (Bourotte et al., 2005; Kong et al., 2010) can be used to identify the influence of combustion sources on PAHs. The total concentrations of COMPAHs in this study for the different sampling sites are ranged from 63.24 ± 17.35 µg/m^3 to 17546.97 ± 1848.55 µg/m^3 accounting for 65% − 83% of total PAHs with the highest mass percentages occurred in RA. The calculated COMPAH/ΣPAH ratios for different sampling sites are 0.65, 0.61, 0.75 and 0.83 for CK, TIMS, AAS, and RA, respectively.

Wu et al. (2014) demonstrated that the total concentrations of COMPAHs cover 42% – 84% and 75%–82% of PAHs associated with $PM_{2.5}$ and PM_{10}, with the highest mass percentages found in Dongsheng (DS) site of sampling area of E'erduosi city in china. This site represents a residential site at the central urban adjacent to a heavy-traffic road.

As an indicator PAHs, BaP was the most carcinogenic PAHs (Johansson and Bavel, 2003 a and b). Its content in this study over the seasonal sampling period varied from 5.7 ± 1.4 µg/m^3 in RA samples to 1657 ± 252 µg/m^3 in CK samples, hold a mean value of 430 ± 66 µg/m^3, accounting for ~ 4% in TIMS to ~ 8% in RA of total PAHs concentrations in the study area. However, the total mass concentrations of the carcinogenic PAHs (∑C-PAHs) (including BaA, CHR, BbF, BkF, BaP, IcdP, DBahA) (USEPA, 1999 and 2009) over the seasonal sampling period in this study are in the range of 32 ± 7 µg/m^3 in RA samples to 9213 ± 1279 µg/m^3 in CK samples with the average concentrations of 2429 ± 344 µg/m^3, accounting for 34–42 % of total PAHs.

PAHs can be classified into lower molecular weight (LMW) containing 2 and 3-ring PAHs, middle molecular weight (MMW) containing 4-ring PAHs and higher molecular weight PAHs (HMW) containing 5 and 6-ring PAHs (Yang et al., 1998 and 2002; Chen et al., 2003 and 2007), and according to tables (2): (5), the mass concentrations of LMW-, MMW-, and HMW-PAHs were in the range of 12.71 ± 1.95 to 9294.54 ± 959.45 µg/m^3, 32.33 ± 8.22 to 9409.73 ± 708.90 µg/m^3, and 31.44 ± 9.27 to 8291.59 ± 1167.57 µg/m^3, respectively. Relatively high proportions of MMW-PAHs (~ 35% – ~ 43%) and HMW-PAHs (~ 31% − ~ 41%) were detected in samples from different sampling sites. Particularly, for CK and TIMS sites, LMW-, MMW-, and HMW-PAHs represent ~ 34%, ~ 38%, ~ 35% and ~ 41%, ~ 31%, ~ 22%, respectively, of the total PAHs, whereas for AAS and RA sites, the MMW-PAHs were predominantly compounds of the total PAHs (i.e. ~ 40% and ~ 43%, respectively) followed by HMW-PAHs accounting for ~ 36% and ~ 41% then LMW-PAHs (i.e. ~ 24% and ~ 17%), respectively.

However, results for the ring distribution of PAHs are comparable to others where 2- and 3-ring PAHs are the dominant form of the PAHs measured in coke manufacturing (Khalili et al., 1995; Yang et al., 1998). You (2008) concluded that 4-ring PAHs were most abundant during coal combustion, accounting for about 80%, 70% and 90% at three individual sampling points. The same conclusion was made by Arditsoglou et al., (2004) that the PAHs were dominated by 4-ring species (48-62%) followed by 3-ring compounds (38-41%) in fly ashes samples from lignite-fired power plants. 5-ring PAHs exhibited equal or even higher contribution respect to 3- and 4-ring species in coke oven stacks (Manoli et al., 2004). Additionally, Ravindra et al., (2006) indicated that the major source for 3- and 4-ring PAHs is coal combustion, while the major source for HMW PAHs (BaP, BbF, BghiP, and Ind) is gasoline vehicles. Therefore, PAHs at the four sites may come mainly from atmospheric transport of the coal combustion and vehicle emissions as both dominated the PAH sources. Regardless, as shown in Figure 5, the total PAHs concentrations (i.e. Total ∑16 PAHs) over the seasonal sampling period for the different sampling sites are well correlated with ∑LMW-PAHs, ∑MMW-PAHs, ∑HMW-PAHs, ∑COMPAHs, ∑C-PAHs over the seasonal sampling period for the different sampling sites with the correlation coefficients higher to 0.99.

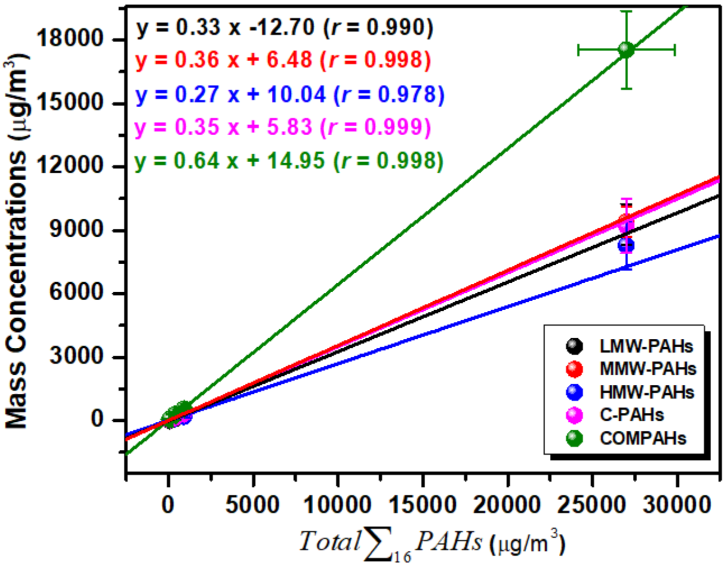

Figure 5. Correlation among total PAHs and LMW-PAHs, MMW-PAHs, HMW-PAHs, C-PAHs and COMPAHs, respectively

Incidentally, it is worth pointing out that the results of PAHs concentrations for this study are generally higher than most of the data reported for some urban areas or even areas proximity to the industrial complexes throughout the world. Table 6 comparing the average PAHs concentrations for some urban areas throughout the world with the data of the RA site.

Table 6. Comparison of mean PAHs concentrations between RA site and other urban sites

Sampling site	**Mean concentration (ng/m^3)**	**Literature**
RA, El-Tabbin city, Egypt	19000	This study
Los Angeles, USA	27	Gordon (1976)
Essen, Germany	1411	Grimmer et al. (1981)
Birmingham, UK	151	Harrison et al. (1996)
Brisbane, Australia	152	Muller et al. (1998)
Seoul, Korea	89	Park et al. (2002)
Chicago, USA	574	Vardar et al. (2004)
Beijing, China	116	Valavanidis et al. (2006)
Athens, Greece	1420	Sharma et al. (2007)
Delhi, India	1782	Esen et al. (2008)
Bursa, Turkey	1410	Chen et al. (2011)
Shanghai, China	216	Zhou et al. (2005)

4. Conclusion

In this study, 16 PAHs in particulate and gaseous phases were identified and quantified in 48 atmospheric air samples from 4 sampling sites in four seasons from January to November 2014 in the south of El-Tabbin city in order to determine the concentration levels, seasonal variations, and their potential sources. The results showed the mass concentration of PAHs with the highest concentrations in the industrial areas (CK, TIMS, and AAS) following by residential area (RA). It was found that PAHs concentrations were high in winter and autumn at the four sampling sites where it takes the order of winter > autumn > spring > summer. This behavior could be attributed to the meteorological factors such as regional climatic conditions, lower atmospheric mixing height, decreased sunlight intensity as well as frequent temperature inversion that intensify the PAH pollution in winter. Atmospheric outflow was estimated based on the concentration of PAHs and wind velocity where the elevated transport fluxes were found during the spring and winter seasons and southeastward transport is dominated. The results of PAHs concentrations for this study were generally higher than most of the data reported for some urban areas or even areas proximity to the industrial complexes throughout the world.

Among the 16 PAHs, FLA, PYR, CHR, BbF, BkF, BaA, BaP, IcdP, BghiP (represent combustion derived PAHs) were most abundant, which reflects the influence of combustion processes (either coal or oil) and vehicle emission. Predominantly coal combustion, vehicle emission (including diesel and gasoline fuel exhaust) and industrial processes are the primary sources for atmospheric PAHs in this heavy-industrialized city. BaP concentration in the study area is extremely high where the average BaP concentration over the seasonal sampling period for the study area, reflecting a serious hidden danger to health.

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