Urban air polycyclic aromatic hydrocarbons: concentrations, summer/winter variation, gas/particle partitioning and health risk assessment at a traffic area

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Abstract

Atmospheric particulate and gaseous polycyclic aromatic hydrocarbons (PAHs) samples were collected from an urban area in Dokki (Giza) during the summer of 2007 and the winter of 2007 - 2008. The average concentrations of PAHs were 1429.74 ng/m³ in the particulate phase, 2912.56 ng/m³ in the gaseous phase and 4342.30 ng/m³ in the particulate + gaseous phases during the period of study. Dokki has high level concentrations of PAH compounds compared with many polluted cities in the world. The concentrations of PAH compounds in the particulate and gaseous phases were higher in the winter and lower in the summer. Total concentrations of PAHs in the particulate phase and gaseous phase were 22.58% and 77.42% in summer and 36.97% and 63.03% in winter of the total (particulate + gaseous) concentrations of PAHs, respectively. The gaseous/particulate (G/P) ratios of PAHs concentration were 3.43 in summer and 1.71 in winter. Significant negative correlation coefficients were found between the ambient temperature and concentrations of the total PAHs in the particulate and gaseous phases. The distribution of individual PAHs and different categories of PAHs based on aromatic ring number in the particulate and gaseous phases during the summer and winter were nearly similar, indicating similar emission sources of PAHs in both two seasons. Benzo(b)fluoranthene in the particulate phase and naphthalene in the gaseous phase were the most abundant compounds. Diagnostic concentration ratios of PAH compounds indicate that these compounds are emitted mainly from pyrogenic sources, mainly local vehicular exhaust emissions. Health risks associated with the inhalation of individual PAHs in particulate and gaseous phases were assessed on the basis of its benzo(a)pyrene equivalent concentration (BaPeq). Dibenzo(a,h)anthracene and benzo(a)pyrene in the particulate phase and benzo(a)pyrene and benzo(a)anthracene in the gaseous phase were the greatest contributors to the total health risks. The mean contributions of the total carcinogenic activity of all PAHs to the total concentrations of PAHs were 29.37% and 25.15% in the particulate phase and 0.76% and 0.92% in the gaseous phase during the summer and winter, respectively. These results indicate that PAHs in the particulate phase in the ambient air of Dokki may pose a potential health risk.

Key words: PAHs, Concentrations, Particulate phase, Gaseous phase, summer/winter variation, Diagnostic ratio, Health risk assessment, Traffic emissions, Urban air, Dokki, Egypt

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. Of various atmospheric contaminants, 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/or mutagenic (Xue and Warshawsky, 2005), and occur mainly in particulate phase in the atmosphere because of their low vapor pressure (Kameda et al., 2005). The low molecular weight PAH compounds are considered to be less harmful to human health than high molecular weight PAH compounds; however, they are able to react with other pollutants such as ozone and NOx to form highly toxic 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). PAHs are semivolatile organic compounds and present in both gaseous and particulate phases in the atmosphere, depending on the vapour 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 behaviour of the compound in the atmosphere (Pankow, 1994; Vardar et al., 2008; Esen et al., 2008). Atmospheric partitioning of PAH compounds between the particulate and the gaseous phases strongly influences their fate and transport in the atmosphere, and the way they enter into human body (Bidleman, 1988; Odabasi et al., 1999). Therefore, evaluation of atmospheric PAHs has received worldwide attention in air pollution studies.

Atmospheric PAHs have diverse sources, with both natural and anthropogenic origins. 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 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 crude oil and petroleum products (kerosene, gasoline, diesel fuel, lubricating oil, and asphalt) contain PAHs and form another important primary source of PAHs are petrogenic source (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/or 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, re-suspended soils and power plants (Binet et al., 2002; Dyke et al., 2003; Zielinska et al., 2004). 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). Particle size distribution of PAHs in the atmosphere revealed that PAHs are usually associated with fine particles (Guo et al., 2003; Bourotte et al., 2005).

There is a lack of information on the levels and distribution of PAH compounds in the gaseous phase in Greater Cairo atmosphere. 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) and dust deposited on leaves of street trees and paved street dust (Khoder, 2007). Therefore, the main objectives of the present study are (i) to evaluate the difference of the environmental concentration levels of PAH compounds in the particulate and gaseous phases during the summer and winter seasons in an urban area (Dokki) in Giza where heavy traffic exists, (ii) to characterize the distribution profiles of the atmospheric PAH compounds in both particulate and gaseous phases, (iii) to assess the effect of ambient air temperature on gas – particle distribution of the atmospheric PAH compounds, (iv) to identify the possible sources of atmospheric PAHs based on diagnostic ratios of PAH compounds, and (v) to evaluate health risks associated with inhalation of PAH compounds in particulate and gaseous phases in the ambient air of the study area.

2. Materials and Methods

2.1. Sampling site and periods

Giza city is very important part of Greater Cairo region due to the presence of the most important Egyptian monuments and historical places in it. It is located along the western side of the River Nile, opposite to the city center of Cairo. Giza lies between two huge industrial areas: Shoubra El-Khiema in the north and Helwan in the southeast. It is located in the subtropical climatic region and characterized by high traffic density. Atmospheric particulate and gaseous PAHs samples were collected from a point approximately 12 m above the ground level at the roof of National Research Centre which is located in the urban area of Giza (Dokki), located to the southwest of the Cairo city centre. The sampling site is characterized by high traffic density and close to the major traffic street in Dokki. One daily sample (24 h) was collected weekly at the sampling location, during the summer season of 2007 (June, July and August) and the winter season of 2007-2008 (December, January and February).

2.2. Sample collection

Atmospheric PAHs samples were collected using a periodically calibrated vacuum pump to draw 5 l/min. The air was drawn through a glass fiber filter (GFF, 7 cm diameter) to collect PAH compounds in the particulate phase and then through adsorbent glass cartridge (ORBO - 1500, Supelco, Inc. Bellefonte, PA) containing a combination of XAD-2 resin (1.5 g) sandwiched between two layers of polyurethane foam (PUF, 30 mm length and 22 mm diameter) to collect PAH compounds present in the gaseous phase. This configuration was used to increase the adsorption capacity and to minimize the post-collection volatilization problems of semivolatile organic compounds (Cindoruk and Tasdemir, 2007; Vardar et al., 2008). Prior to air sample collection, a cleaning procedures were applied to GFFs and adsorbent PUF/ XAD-2 glass cartridges. The GFFs were combusted at 450 ⁰C for 12 h to remove organic impurities and allowed to cool to room temperature in desiccators, and then stored in aluminum foil packages until used. PUF/XAD-2 glass cartridges were cleaned by sequential Soxhlet extractions with distilled water, methanol, dichloromethane (DCM) and a mixture of DCM/n-hexane (50/50, v/v) for 24 h in turn and finally dried in a clear oven at 45 °C to remove residual solvent according to Fang et al. (2004a). After cleaning processes, each end of the PUF/XAD-2 glass cartridges was capped quickly with polypropylene caps and placed in a sealed glass jars and stored in plastic bags until used. Cleaned and prepared GFFs and PUF/XAD-2 glass cartridges were transported to the field in their containers without allowing exposure to the ambient air. After sampling time, the PUF/XAD-2 glass cartridges was removed from the sampling train and the two open sides were tightly closed using polypropylene caps and placed in a sealed glass jars and finally stored in plastic bags in a freezer until analyzed. In addition, GFFs were stored in aluminum foil packages sealed in plastic bags in a freezer until analyzed. In the present study, particulate PAH compounds are defined as those collected on the GFFs, whereas gaseous PAH compounds are defined as those collected on the two layers of PUF and XAD-2 resin.

2.3. Sample extraction and analysis

For PAH extraction from the samples, the GFFs and PUF/XAD-2 glass cartridges were placed separately in appropriate Soxhlet apparatus and extracted with DCM/n-hexane mixture (50/50, v/v) for 24 h according to Fang et al. (2004c). The organic extracts were then concentrated using a rotary evaporator, cleaned by clean silica gel/alumina columns consisting of 5 g anhydrous sodium sulfate, 20 g silica gel (deactivated 5% with distilled water), 10 g alumina (deactivated 1% with distilled water), 5 g sand, and glass wool according to Park et al. (2001). The extracts were concentrated, exchanged to 2 ml hexane, placed on the columns, and eluted with 1:1 pentane-dichloromethane (200 ml). The eluted extracts were concentrated on a rotary evaporator and exchanged to 1 ml hexane and stored in a freezer till analysis. For PAHs analysis, all extracts were analyzed using a gas chromatography (GC) (Hewlett- Packard HP6890) fitted with a Flame lonization Detector (FID). A HP-5 (30 m x 320 μ m x 0.25 μ m) capillary column with hydrogen as carrier gas was used. GC/FID was calibrated with a diluted

standard solution of 15 compounds (PAH mixture, Supelco, Inc., Bellefonte, PA), and the concentrations of the target PAH compounds were quantified using this external standard solution. The concentrations of the following PAH compounds in the particulate and gaseous phases were determined: naphthalene (NA), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CRY), benzo(b)fluoranthene (BbF), benzo(a)pyrene (BaP), dibenzo(a,h)anthracene (DBA), benzo(ghi)perylene (BGP), and indeno(1, 2, 3,- cd)pyrene (IND).

3. Results and Discussion

3.1. Particulate and gaseous PAHs concentrations in the ambient air of Dokki

PAH compounds can be classified by their number of aromatic rings as follows: two aromatic rings including NA; three aromatic rings including ACY, ACE, FLU, PHE and ANT; four aromatic rings including FLT, PYR, BaA and CRY; five aromatic rings including BbF, BaP and DBA; six aromatic rings including IND and BGB. Atmospheric concentrations of the individual PAH compounds and different categories of PAHs based on ring number in the particulate and gaseous phases during the period of study are shown in Table 1. From this table, it can be noticed that significant compositional differences were observed between the particulate and gaseous phases. BbF, BGP, DBA and CRY were the most abundant PAH compounds in the particulate phase with an average concentrations of 222.39, 214.79, 171.53 and 166.91 ng/m³, respectively. Based on aromatic ring number, PAH compounds with five aromatic rings were the highest concentration (544.97 ng/m³), followed by four aromatic rings (422.86 ng/m³), six aromatic rings (334.02 ng/m³), three aromatic rings (111.22 ng/m³) and two aromatic rings (16.67 ng/m^3) . For gaseous phase, the predominant PAH compounds were NA, FLU, ACY and ACE with an average concentrations of 851.59, 483.22, 429.36 and 356.60 ng/m³, respectively (Table 1). In addition, PAH compounds with three aromatic rings were of the highest concentration (1663.32 ng/m³), followed by two aromatic rings (851.59 ng/m³), four aromatic rings (369.57 ng/m³), five aromatic rings (19.43 ng/m^3) and six aromatic rings (8.38 ng/m^3) .

The mean relative contribution of each individual PAH compound and different categories of PAHs based on aromatic ring number to the total concentrations of PAH compounds in the particulate and gaseous phases during the period of study are represented graphically in Figure 1. From this figure, it can be observed that the BbF (15.56%) was the predominant PAH compound in the particulate phase. The distribution of individual PAH compounds in the gaseous phase were generally decreased with increasing molecular weight. Based on aromatic ring number, the mean distribution of PAHs in the particulate and gaseous phases indicate that the PAH compounds with four to six aromatic rings were the predominant in the particulate phase, whereas PAH compounds with two to three aromatic rings were the predominant in the gaseous phase during the period of study (Figure 1b). These results are in

good agreement with the theoretical fact that the higher molecular weight PAHs are generally less volatile and attached to the particulate phase while the reverse is true for the lower molecular weight PAHs which are usually found in the gaseous phase (Fang et al., 2004a). The distribution of PAH compounds in the particulate and gaseous phases depends on molecular weight (Odabasi et al., 1999; Cincinelli et al., 2007). The predominant PAH compounds in the particulate phase were the four to six PAH rings (Fon et al., 2007; Kishida et al., 2008). PAH compounds with two to three aromatic rings were detected predominantly in the gaseous phase (Ohura et al., 2004).

In the present study, the total (particulate + gaseous) PAH concentrations of each individual compound and different categories of PAHs based on aromatic ring number during the period of study are represented graphically in Figure 2. From this figure, it can be seen that NA (868.26 ng/m³), FLU (503.59 ng/m³), ACY (448.19 ng/m³), and ACE (378.31 ng/m³) were the most abundant compounds and represent 20.00, 11.61, 10.32 and 8.71% of the total concentration of PAH compounds, respectively. In addition, PAH compounds with three aromatic rings (1774.54 ng/m³) were the predominant followed by two aromatic rings (868.26 ng/m³), four aromatic rings (792.43 ng/m³), five aromatic rings (564.67 ng/m³) and six aromatic rings (342.4 ng/m³) and accounted for 40.87, 20.00, 18.25, 13.00 and 7.88% of the total (particulate + gaseous) concentration of PAH compounds, respectively.

The total concentrations of PAH compounds in the particulate and gaseous phases, and their relative contribution to the total (particulate + gaseous) PAHs concentrations in the ambient air of the study area are shown in Table 2. The average total concentrations of the PAH compounds were 1429.74, 2912.56 and 4342.30 ng/m³ in the particulate phase, gaseous phase, and particulate + gaseous phases, respectively, during the period of study. The relative contribution of the total concentrations of PAH compounds in the particulate and gaseous phases to the total (particulate + gaseous) PAH concentrations were 32.93 and 67.07%, respectively. In addition, the gaseous/particulate (G/P) ratio of the total PAHs concentrations was 2.04 during the period of study. This (G/P) ratio was nearly similar to that found in an urban area of the North Chinese Plain (~ 2, Liu et al., 2008) and much lower than those found in Birmingham, UK (5 – 6, Harrison et al., 1996), in Guangzhou (>10, Li et al., 2006) and in Kozani, Greece (~ 10, Terzi and Samara, 2004). In the present study, the average of total PAHs concentration (1429.74 ng/m^3) in the particulate phase was lower than those found in Greater Cairo (3402.8 ng/m^3) in the city centre of Cairo and 1904.2 ng/m³ in Faysal, Giza, Hassan, 2006) and in Taiyuan city (1504.7 ng/m³, Peng et al., 2003) and higher than that found in New Delhi, India (891 ng/m³, Sharma et al., 2007). The average total (particulate + gaseous) PAHs concentrations of each individual compound in the urban area of Giza (Dokki) were compared with those found in different locations all over the world (Khalili, 1992; Halsall et al., 1994; Odabasi et al., 1999; Lin et al., 2002; Poor et al., 2004; Fang et al., 2004c; Tsapakis and Stephanou, 2005; Li et al., 2006; Tasdemir and Esen, 2007). As shown in Table 3, it can be seen clearly that the average total (particulate + gaseous) PAH concentrations of each individual compound and total PAH compounds in the urban area of Giza were much higher when compared with those reported in other cities all over the world. These results clearly indicate that the urban area of Giza (Dokki) is one of the most PAHs contaminated areas in the world.

3.2. Seasonal variations of PAHs concentrations in the particulate and gaseous phases

Atmospheric concentrations of the individual PAH compounds and different categories of PAHs based on aromatic ring number in the particulate and gaseous phases during the summer and winter seasons are shown in Table 4. From this table, it can be seen that the highest concentrations of PAH compounds in the particulate phase were found in the winter, whereas the lowest levels were detected in the summer, and the differences in mean concentrations were statistically significant (p < 0.001). The concentrations of the individual PAH compounds in the particulate phase ranged from 4.23 ng/m³ for NA to 97.01 ng/m³ for BbF (with a total PAHs value of 550.47 ng/m³) in the summer and from 29.09 ng/m³ for NA to 348.35 ng/m³ for BbF (with a total PAHs value of 2309.99 ng/m³) in the winter season. In addition, the concentrations of PAH compounds with two aromatic rings, three aromatic rings, four aromatic rings, five aromatic rings and six aromatic rings in the particulate phase were 4.23, 30.28, 137.75, 238.97 and 139.24 ng/m³ in the summer and 29.09, 192.14, 708.06, 851.88 and 528.80 ng/m³ in the winter, respectively. For gaseous phase, the highest concentrations of PAH compounds were also found in the winter, whereas the lowest levels were detected in the summer, and the differences in mean concentrations were statistically significant (p < 0.001). The concentrations of the individual PAH compounds in the gaseous phase ranged from 2.42 ng/m³ for IND to 603.51 ng/m³ for NA (with a total PAHs value of 1887.77 ng/m³) in the summer and from 4.08 ng/m³ for DBA to 1100.00 ng/m³ for NA (with a total PAHs value of 3939.06 ng/m^3) in the winter season. Moreover, the total concentrations of PAH compounds were 603.51 and 1100.00 ng/m³ for two aromatic rings, 1118.45 and 2210.67 ng/m³ for three aromatic rings, 148.03 and 590.62 ng/m³ for four aromatic rings, 12.53 and 26.26 ng/m³ for five aromatic rings and 5.25 and 11.50 ng/m³ for six aromatic rings in the summer and winter seasons, respectively (Table 4). For particulate + gaseous phase, the total (particulate + gaseous) concentrations of the individual PAH compounds ranged from 50.78 ng/m³ for IND to 607.42 ng/m³ for NA (with a total PAHs value of 2438.24 ng/m³) in the summer and from 195.40 ng/m³ for IND to 1129.09 ng/m³ for NA (with a total PAHs value of 6249.05 ng/m^3) in the winter (Figure 3). These results clearly indicate that the concentrations of PAHs in the particulate phase, gaseous phase and total (particulate + gaseous phases) were higher in the winter and lower in the summer season. This finding is consistent with those of previous investigators who found that the highest concentrations of PAH compounds were in winter season (Terzi and Samara, 2004; Hassan, 2006; Cincinelli et al., 2007; Fon et al., 2007; Sharma et al., 2007; Esen et al., 2008; Liu et al., 2008; Vardar et al., 2008).

Winter/summer (W/S) concentration ratios for the individual PAH compounds and different categories of PAHs based on aromatic ring number in the particulate phase, gaseous phase and total (particulate + gaseous phases) are given in Table 5. The W/S concentration ratios for the individual PAH compounds ranged from 3.27 for BaP to 7.59 for ACE in the particulate phase, from 1.46 for DBA to 4.36 for BaA in the gaseous phase and from 1.86 for NA to 4.85 for CRY in the total (particulate + gaseous phases). Based on aromatic ring number, W/S concentration ratios were 6.88, 6.35, 5.14, 3.56 and 3.80 in the particulate phase, 1.82, 1.98, 3.99, 2.10 and 2.19 in the gaseous phase and 1.86, 2.10, 4.56, 3.50 and 3.74 in the total (particulate + gaseous phases) for PAH compounds with two aromatic rings, three aromatic rings, four aromatic rings, five aromatic rings and six aromatic rings, respectively (Table 5). In addition, W/S concentration ratios for the total PAH compounds were 4.20, 2.10 and 2.56 in the particulate phase, gaseous phase and total (particulate + gaseous phases), respectively. Although W/S concentration ratio reflects the characteristics of a city, its meteorological conditions and sources of PAH specific to that city, it would be instructive to compare the W/S concentration ratios in the present study with those found in different cities around the world. The particulate PAH compounds in winter were generally higher by a factor of 1.74 - 8.60 than that in summer in Naples- Italy and New Delhi-India (Caricchia et al., 1999; Sharma et al., 2007). The W/S concentration ratios were 38 for the particulate PAHs phase and 7.4 for the gaseous PAHs phase (Esen et al., 2008). The W/S concentration ratios for the gaseous and particulate PAHs phases were 1.80 and 8.00, respectively (Liu et al., 2008). Total concentrations of each individual PAH compound in winter were approximately 8 - 30 times higher than those found in summer season (Vardar et al., 2008).

The seasonal variations in PAHs concentrations in the atmosphere depend on several factors, such as meteorological conditions, photochemical degradation and radical reactions (Ohura et al., 2004; Lima et al., 2004). The general climate of Giza city is characterized by high temperature, high solar radiation, clear sky and rainless in summer, whereas it is cold, moist and rainy in winter. Therefore, low dispersive conditions during winter due to the reduction of the thermal turbulence under the effect of low temperature trap PAHs pollutant over the study area for long periods, and consequently increasing the levels of these pollutants during that season. On the other hand, the lower concentrations of PAH compounds during summer may be due to the high dispersion and high dilution conditions under the effect of high temperature, which increases the thermal turbulence currents during this season. The relationship between the ambient temperature and concentrations of the total PAH compounds in Figure 4. From this figure, it can be noticed that, significant negative correlation coefficients were found between the ambient temperatures of the total PAH compounds in particulate and gaseous phases (r = - 0.98, p < 0.001 for particulate PAHs and r = - 0.93, p < 0.001 for gaseous PAHs). These negative correlation coefficients clearly indicate that the concentrations of the total PAH compounds in

both particulate and gaseous phases decrease with increasing temperature. This finding is consistent with those of previous investigators who found negative correlations between the ambient temperature and concentrations of the total PAH compounds in the particulate and gaseous phases (Tsapakis and Stephanou, 2005; Fon et al., 2007; Cincinelli et al., 2007). In Giza city, higher temperature degrees and higher solar radiation intensity during summer lead to an increasing in the photochemical reactions and consequently an increasing in the formation of ozone, photochemical oxidants and radicals such as OH and NO₃. Previous studies on the seasonal variation of ozone concentration in urban areas in Giza had observed that the highest levels of ozone were in summer and the lowest levels were in winter (Khoder, 2009). Therefore, the lower levels of PAH compounds during summer in the present study may be due to the higher levels of ozone, photochemical oxidants and radicals such as OH and NO₃. Under the effect of higher photochemical reactions, an increase in the photodecomposition of PAH compounds usually occur. Consistent with the observations of previous investigators, reduced chemical and photochemical degradation, due to lower sunlight intensity and temperature, and differences in ozone level can contribute to the higher PAH concentrations in winter than in summer season (Kiss et al., 1998; Esen et al., 2008). Negative correlation was found between the concentrations of PAH compounds and ozone (Tsapakis and Stephanou, 2005). High temperature along with enhanced photodecomposition of PAHs in summer leads to a decrease in the concentration of PAHs (Cincinelli et al., 2007; Sharma et al., 2007).

The distribution of PAH compounds between gaseous and particulate phases is dependent upon temperature, air humidity, property of adsorption surface, available adsorption surface, molecular weight and vapour pressure of PAHs (Masclet et al., 1986). The mean contribution of the total concentrations of PAH compounds in the particulate phase and gaseous phase to the total (particulate + gaseous) concentrations of PAH compounds were 22.58% and 77.42% in summer and 36.97% and 63.03% in winter, respectively (Table 2). In addition, the gaseous/particulate (G/P) ratios of PAHs concentration were 3.43 in summer and 1.71 in winter. The higher contribution of particulate PAHs to the total (particulate + gaseous) PAHs concentrations in addition to the lower G/P ratio of PAHs concentration in the winter than in the summer may be attributed to the lower temperature during the winter, which made favourable conditions for the condensation/adsorption of these species on suspended particulate matter present in air. This is in agreement with Kiss et al. (1998) who reported that the gas - to - particle distribution of PAHs can be shifted towards the particle phase at lower temperature and sunlight intensity. The increase in the gas - to - particle conversion at lower temperature and stable conditions in the winter leads to an increase in the particulate PAHs during that season (Sharma et al., 2007). On the other hand, the contribution of gaseous PAHs to the total (particulate + gaseous) PAHs concentration and G/P ratio of PAHs concentration in the present study were higher in the summer than in the winter season. This may be due to an increase in the gas -

particle partitioning since compound vapour pressures increase with increasing temperature (Sonnefeld et al., 1983). High ambient temperature could change the distribution of PAH compounds between the particulate and gaseous phases by increasing the vapour pressure of these pollutants that adhered to particulate matter in the atmosphere and favouring the volatilization of PAHs from the particulate to gaseous phase (Sin et al., 2003). Although high atmospheric temperature increases the conversion of PAH compounds from particulate to gaseous phase, the levels of PAHs in gaseous phase in the present study decreased from winter to summer and also with increasing temperature (Figure 4). This can be explained by the increase in the mixing height of the atmosphere of the study area under the effect of higher temperature and hence the reduction in the levels of gaseous PAHs. In addition, the decreasing in gaseous PAHs levels from winter to summer may be also due to the increase in the photochemical reactions with OH and NO3 radicals in summer relative to winter which could cause more photodegradation of gaseous PAHs (Bahm and Khalil, 2004). Gas - phase reactions with OH are believed to be the dominant loss process for volatile PAHs (Atkinson and Arey, 1994). The mean contribution of the total gaseous PAHs concentrations to the total (particulate + gaseous) PAHs concentrations (63.03% in winter and 77.42% in summer) in the present study were lower than those found in Bursa, Turkey (66% in winter and 89% in summer) (Vardar et al., 2008) and in Guangzhou, South China (98.2% in summer) (Li et al., 2006), whereas the contribution of the total gaseous PAHs in winter was higher than that found in Guangzhou, South China (53.80% in winter) (Li et al., 2006).

3.3. Particulate and gaseous PAHs distribution and possible sources

The mean relative distribution of the individual PAH compounds and different categories of PAHs based on aromatic ring number in the particulate and gaseous phases during the summer and winter season are illustrated in Figures 5 and 6, respectively. From these figures, it is clear that the distribution of individual PAH compounds and different categories of PAHs in summer and winter were nearly similar, indicating similar emission sources of PAHs in the urban area of Giza during both two seasons; vehicle exhaust emissions are the dominant one. BbF, BGP, CRY, DBA and BaP were the most dominant PAH compounds in the particulate phase during the summer and winter. These compounds accounted for 70.01% (summer) and 63.59% (winter) of the total particulate PAH compounds. For gaseous phase, NA, FLU, ACY and ACE were the most dominant PAH compounds during the summer and winter seasons. These compounds accounted for 76.87% (summer) and 70.89% (winter) of the total gaseous PAH compounds (Figures 5a and 6a). Based on aromatic ring number, PAH compounds with four to six aromatic rings were the dominant PAH compounds in the particulate phase don aromatic ring number, PAH compounds with relative contribution of 93.73% in summer and 90.42% in winter, whereas PAH compounds with two and three aromatic rings were detected predominantly in the gaseous phase with relative contribution of 91.22% in summer and 84.05% in winter (Figures 5b and 6b).

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Ratios of the individual PAH compounds in the particulate phase are frequently utilized as diagnostic tools to distinguish and determine the possible sources of atmospheric PAHs measured at the study area (Harrison et al., 1996; Bourotte et al., 2005). Most commonly used ratios are phenanthrene to anthracene (PHE/ANT), anthracene to anthracene + phenanthrene [ANT/(ANT + PHE)], fluoranthene to pyrene (FLT/PYR), fluoranthene to fluoranthene + pyrene [FLT/(FLT + PYR)], benzo(a)pyrene to benzo(ghi)perylene (BaP/BGP), benz(a)anthracene to chrysene (BaA/CRY) and indeno(1,2,3-cd)pyrene to benzo(ghi)perylene (IND/BGP). Diagnostic concentration ratios of selected PAH compounds obtained in this study are shown in Table 6. Using the ratio of a more reactive PAH to less reactive PAH gives very useful information not only for source identification and photochemical degradation of PAHs but also about the aging of the air mass (Lohmann et al., 2000; Ding et al., 2007). The concentration ratio of BaA/CHR is regarded as an indicator of aging air masses; aging of atmospheric aerosol. Higher BaA/CHR concentration ratio than 0.40 indicate freshly emitted pollution and relatively little photochemical processing of the air mass, whereas lower ratio than 0.40 indicates that major sources of PAHs are not local or the air masses are aged (Lohmann et al., 2000).

In the present study, the mean concentration ratios of BaA/CHR were 0.64, 0.59 and 0.60 in the summer, winter and total period of study, respectively (Table 6), indicating freshly emitted PAHs from local sources or the air masses are not aged. The mean concentration ratios of [FLT/(FLT + PYR)] were 0.61, 0.59 and 0.60 in the summer, winter and total period of study, respectively (Table 6), suggesting that PAH emissions were due to fossil fuel combustion (Yunker et al., 2002). The concentration ratios of BaA/CRY and BaP/BGP are used to investigate the emission sources of PAHs. BaA/CRY concentration ratio was 0.53 ± 0.06 for motor vehicle emissions (Dickhut et al., 2000). BaP/BGP concentration ratio higher than 0.60 also refers to the presence of traffic emissions (Park et al., 2002). The mean concentration ratios of BaA/CRY and BaP/BGP were 0.64 and 0.77 in summer, 0.59 and 0.68 in winter and 0.60 and 0.70 during the period of study, respectively (Table 6). These ratios imply that the atmospheric PAHs were more influenced by vehicular exhaust emissions than other sources. The concentration ratios of IND/BGP and BaA/CRY are used to identify the traffic sources. Caricchia et al. (1999) reported that the IND/BGP concentration ratio for gasoline engines is about 0.40, while the ratio for diesel engine approaches 1.00. The concentration ratios of BaA/CRY ranged from 0.28 to 1.20 for gasoline engines and from 0.17 to 0.36 for diesel engines (Fang et al., 2004a; Bourotte et al., 2005). In the present study, the mean concentration ratios of IND/BGP and BaA/CRY were 0.53 and 0.64 in summer, 0.56 and 0.59 in winter and 0.55 and 0.60 during the period of study, respectively, indicating more contribution of gasoline vehicles rather than diesel vehicles.

The concentration ratios of PHE/ANT and FLT/PYR have been used as a characteristic diagnostic parameter for PAHs emitted from petrogenic versus pyrogenic sources. A PHE/ANT concentration ratio of less than 10 and FLT/PYR concentration ratio of greater than 1.00 indicate that PAHs come from

pyrogenic source and PHE/ANT concentration ratio of greater than 15.00 and FLT/PYR concentration ratio of less than 1.00 indicate petrogenic origins of PAHs (Baumard et al., 1998). In the present study, the mean concentration ratios of PHE/ANT and FLT/PYR were 1.19 and 1.59 in summer, 1.29 and 1.46 in winter and 1.27 and 1.48 during the period of study, respectively (Table 6). These results indicate that pyrogenic source was the predominant sources of PAHs in the study urban area in Giza. In addition, the concentration ratio of ANT/ (ANT + PHE) is used to estimate the presence of PAHs from fossil fuels inputs (Yunker et al., 2002). Thus, if the above ratio is lower than 0.1 this will be an indication of nonburned fossil fuel inputs, while if the ratio is higher than 0.1, combustion sources may prevail. In the present study, the mean concentration ratios of ANT/ (ANT + PHE) were 0.46, 0.44 and 0.44 during the summer, winter and total period of study, respectively, indicating combustion related emission sources. The ratio of the sum of concentrations of combustion related non-alkylated PAHs (CPAHs = FLT, PYR, BaA, CRY, BbF, BaP, IND and BGP) to the total PAHs (CPAHs/ Σ PAHs) has been used as a characteristic diagnostic parameter for PAHs emitted from stationary versus mobile combustion sources, with values of CPAHs/SPAHs < 1 for particulate PAHs from mobile sources (Rogge et al., 1993). The mean concentration ratios of CPAHs/SPAHs were 0.81, 0.79 and 0.79 in the particulate phase in the study urban area in Dokki (Giza) during the summer, winter and total period of study, respectively. This result indicates that combustion, rather than unburned fossil fuels, is the principal PAHs contributor to the Dokki atmosphere.

3.4. Environmental health risk assessment of PAHs in the particulate and gaseous phases

Benzo(a)pyrene (BaP) is known to be the most potent carcinogenic PAH (Wang et al. 2002). It has been regarded by the World Health Organization (WHO, 1987) as a good index for whole PAH carcinogenicity. In addition, B(a)P is often used as a marker for total PAHs exposure in the environment (Lin et al., 2002). About 88% of the ambient BaP in British cities was estimated to come from road traffic using principle component and multi-linear regression analyses (Harrison et al., 1996). Therefore, BaP has often been used as a key indicator for PAHs risk assessment in urban atmosphere. In the present study, the average concentrations of BaP were 70.74, 231.58 and 151.05 ng/m³ in the particulate phase and 4.98, 11.99 and 8.50 ng/m³ in the gaseous phase during the summer, winter and total period of study, respectively. These concentrations are highly exceeding the guided levels of BaP in Italy (1.00 ng/m³) (Menichini et al., 1999) and the recommended level (0.25 ng/m³) that had been put forward for consultation in Britain (Lim et al., 1999).

The health risk associated with inhalation of carcinogenic PAH compounds in the study area was estimated by using Toxic Equivalent Factors (TEFs) for individual PAH compounds. These factors have been devised as a means of comparing the carcinogenicity of the individual PAH compounds to the carcinogenicity of BaP (Petry et al., 1996). The cancer potency of each PAH compound was assessed on

the basis of its benzo(a)pyrene equivalent concentration (BaPeq). The BaPeq concentrations for the individual PAH compounds were calculated by multiplying the individual PAH concentration by its corresponding TEF value (Nisbet and La Goy, 1992; Fang et al., 2004b). BaPeq concentrations of the individual PAH compounds in the particulate phase ranged from 0.004 ng/m³ for NA to 71.22 ng/m³ for DBA during summer, 0.029 ng/m³ for NA to 271.95 ng/m³ for DBA during winter and 0.017 ng/m³ for NA to 171.53 ng/m³ for DBA during the period of study (Table 7). For gaseous phase, BaP_{eq} concentrations of the individual PAH compounds ranged from 0.028 ng/m³ for BGP to 4.98 ng/m³ for BaP during summer, 0.062 ng/m³ for BGP to 12.21 ng/m³ for BaA during winter and 0.045 ng/m³ for BGP to 8.50 ng/m³ for BaP during the period of study (Table 7). In addition, the total carcinogenic activity (TCA) of all measured PAH compounds were 161.69, 580.98 and 371.14 ng/m³ in the particulate phase and 14.30, 36.31 and 25.32 ng/m³ in the gaseous phase during the summer, winter and total period of study, respectively (Table 7). The relative contribution of the carcinogenic activity for each individual PAH compounds in the particulate phase indicate that DBA and BaP were the most dominant compounds, these accounted for 44.05% and 43.75% (summer), 46.81% and 39.86% (winter) and 46.22% and 40.69% (during the period of study) of the total carcinogenic activity of all PAH compounds measured, respectively. For gaseous phase, BaP and BaA compounds exhibited the highest contribution and accounted for 34.83% and 19.58% (summer), 33.02% and 33.63% (winter) and 33.57% and 29.64% (during the period of study) of the total carcinogenic activity of all PAH compounds measured, respectively (Table 7). These results show the importance of DBA and BaP in particulate phase and BaP and BaA in gaseous phase as a surrogate compounds for PAHs in the atmosphere of the study area (Dokki). However, other PAH compounds including BbF, IND and BaA in the particulate phase and DBA, BbF and IND in gaseous phase also play a role in the total carcinogenicity of PAH compounds in Dokki air.

The risk of inhaling carcinogenic PAH compounds depends on whether the PAH compounds enter the lungs in gaseous form or whether they are inhaled on particulate matter which penetrate into the lungs and exert their carcinogenicity over long periods of time. The relative contribution of the total carcinogenic activity of all PAH compounds (TCA) to the total concentrations of PAH compounds were 29.37%, 25.15% and 25.96% in the particulate phase and 0.76%, 0.92% and 0.87% in the gaseous phase during the summer, winter and total period of study, respectively. The higher contribution of the total carcinogenic activity (TCA) in the particulate phase than in the gaseous phase indicate that the particulate PAH compounds are considered to be the most hazardous substances to human health. Although the gaseous PAH compounds have weaker carcinogenic activity, their concentrations were higher than particulate PAH compounds in the atmosphere of Dokki. The lighter PAH compounds in the gaseous phase which are the most abundant in the atmosphere react with other pollutants to form more toxic derivatives.

Conclusions

Particulate and gaseous PAHs concentrations in ambient air samples collected during the summer and winter seasons in an urban area (Dokki) of Giza were measured while their seasonal variations, their correlation with ambient temperature, their gas/particle distribution, their sources and their health risk assessment were characterized. The results of the analysis showed that the average total concentrations of PAHs were 1429.74, 2912.56 and 4342.30 ng/m³ in the particulate phase, gaseous phase and particulate + gaseous phases, respectively, during the period of study. The level concentrations (particulate + gaseous) of the individual PAH compound and total PAH compounds were much higher than those found in different polluted cities in the world. Winter/summer concentration ratios for the total PAH compounds were 4.20, 2.10 and 2.56 in the particulate phase, gaseous phase and total (particulate + gaseous phases), respectively. The mean contribution of the total concentrations of PAH compounds in the particulate phase and gaseous phase to the total (particulate + gaseous) concentrations of PAH compounds were 22.58% and 77.42% in summer and 36.97% and 63.03% in winter, respectively. In addition, the gaseous/particulate ratios of PAHs concentration were 3.43 in summer and 1.71 in winter. The concentrations of the total PAH compounds in both particulate and gaseous phases decrease with increasing ambient air temperature. BbF, BGP, CRY, DBA and BaP were the most dominant PAH compounds in the particulate phase, whereas NA, FLU, ACY and ACE were the most dominant PAH compounds in the gaseous phase during the summer and winter seasons. In addition, PAH compounds with four to six aromatic rings were the dominant PAH compounds in the particulate phase with relative contribution of 93.73% in summer and 90.42% in winter, whereas PAH compounds with two to three aromatic rings were detected predominantly in the gaseous phase with relative contribution of 91.22% in summer and 84.05% in winter. Based on the diagnostic concentration ratios, it was concluded that combustion, rather than unburned fossil fuels, constitutes the main sources of PAHs. In addition, local vehicular exhaust emissions are the dominant sources of PAHs in Dokki atmosphere during the period of study. BaPeq concentrations of the individual PAH compounds ranged from 0.017 ng/m³ for NA to 171.53 ng/m³ for DBA in the particulate phase and from 0.045 ng/m³ for BGP to 8.50 ng/m³ for BaP in the gaseous phase during the period of study. DBA and BaP in the particulate phase and BaP and BaA in the gaseous phase are considered a surrogate compounds for PAHs in the atmosphere of the study area. Total carcinogenic activity of all measured PAH compounds during the period of study accounted for 25.96% and 0.87% of the total concentrations of PAHs in the particulate and gaseous phases, respectively. These results indicate that particulate PAHs in the ambient air of Dokki may pose a potential health risk. However, the lighter PAH compounds in the gaseous phase which are the most abundant in the atmosphere of the study area also play a role in health risk since they can react with other pollutants to form more toxic derivatives.

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DAIL	Particulate phase	hase Gase Mean \pm SD ^a Rang 16.67 \pm 13.05 432. 16.67 \pm 13.05 432. 16.67 \pm 13.05 432. 18.83 \pm 14.85 203. 21.71 \pm 17.53 183. 20.37 \pm 16.07 214. 28.17 \pm 20.96 115. 22.14 \pm 15.98 73.8 69 111.22 \pm 85.38 797. 30 92.50 \pm 67.16 38.6 56 62.52 \pm 46.80 37.9 14 100.93 \pm 68.86 20.0 91 166.91 \pm 116.99 12.6 71 422.86 \pm 299.82 109. 98 222.39 \pm 132.16 3.61 93 151.05 \pm 85.66 3.78 95 171.53 \pm 106.16 1.99 7.96 544.97 \pm 323.57 9.38 15 119.23 \pm 74.55 1.62 15 214.79 \pm 130.53 2.03 30 334.02 \pm 204.91 3.65	Gaseous phase	Gaseous phase			
PAH compounds	Range	Mean \pm SD ^a	Range	Mean ± SD			
Naphthalene (NA)	2.18 - 36.94	16.67 ± 13.05	432.66 - 1355.00	851.59 ± 285.29			
$\sum 2$ -ring PAHs ^b	2.18 - 36.94	16.67 ± 13.05	432.66 - 1355.00	851.59 ± 285.29			
acenaphthylene (ACY)	2.55 - 42.52	18.83 ± 14.85	203.11 - 702.18	429.36 ± 158.23			
Acenaphthene (ACE)	2.77 - 50.04	21.71 ± 17.53	183.22 - 580.32	356.60 ± 122.77			
Fluorene (FLU)	2.80 - 45.78	20.37 ± 16.07	214.48 - 808.19	483.22 ± 197.78			
Phenanthrene (PHE)	4.92 - 61.69	28.17 ± 20.96	115.95 - 367.10	229.01 ± 79.34			
Anthracene (ANT)	4.28 - 48.66	22.14 ± 15.98	73.84 - 275.08	165.13 ± 63.09			
\sum 3-ring PAHs ^c	17.68 - 248.69	111.22 ± 85.38	797.15 - 2732.87	1663.32 ± 620.42			
Fluoranthene (FLT)	15.93 - 192.80	92.50 ± 67.16	38.62 - 247.22	124.29 ± 76.28			
Pyrene (PYR)	11.38 - 133.56	62.52 ± 46.80	37.94 - 250.76	125.57 ± 79.83			
Benz(a)anthracene (BaA)	24.51 - 209.44	100.93 ± 68.86	20.01 - 153.06	75.06 ± 49.95			
Chrysene (CRY)	37.47 - 343.91	166.91 ± 116.99	12.63 - 90.22	44.65 ± 29.39			
\sum 4-ring PAHs ^d	90.99 - 879.71	422.86 ± 299.82	109.20 - 741.26	369.57 ± 235.38			
Benzo(b)fluoranthene (BbF)	79.91 - 423.08	222.39 ± 132.16	3.61 - 12.74	7.49 ± 2.99			
Benzo(a)pyrene (BaP)	52.56 - 287.93	151.05 ± 85.66	3.78 - 14.90	8.50 ± 3.82			
Dibenzo(a,h)anthracene (DBA)	50.86 - 336.95	171.53 ± 106.16	1.99 - 4.90	3.44 ± 0.85			
∑5-ring PAHs ^e	183.83 - 1047.96	544.97 ± 323.57	9.38 - 32.54	19.43 ± 7.62			
Indeno(1, 2, 3,-cd)pyrene (IND)	33.93 - 228.15	119.23 ± 74.55	1.62 - 6.85	3.85 ± 1.61			
Benzo(ghi)perylene (BGP)	64.61 - 406.45	214.79 ± 130.53	2.03 - 7.97	4.53 ± 1.89			
\sum 6-ring PAHs ^f	99.14 - 634.60	334.02 ± 204.91	3.65 - 14.82	8.38 ± 3.51			

Table 1. Atmospheric concentrations (ng/m^3) of the individual PAH compounds and different categories of PAHs based on aromatic ring number in the particulate and gaseous phases during the period of study

^aStandard deviation, ^bTotal 2-ring PAH compound, ^cTotal 3-ring PAH compounds, ^dTotal 4-ring PAH compounds, ^eTotal 5-ring PAH compounds, ^fTotal 6-ring PAH compounds

Table 2. Average of total concent	rations (ng/m ³) of PA	H compounds in the	particulate and gas	seous phases and the	ir
relative contribution to the total (particulate + gaseous)	PAH concentrations	in the ambient air	of the study area	

	Total PAHs conce	entration (ng/m ³)	Relative contribution (%)			
	Particulate phase	Gaseous phase	Particulate + gaseous phases	Particulate phase	Gaseous phase	
Summer	550.47	1887.77	2438.24	22.58	77.42	
Winter	2309.99	3939.06	6249.05	36.97	63.03	
All period	1429.74	2912.56	4342.30	32.93	67.07	

of each mu	viuuai c	ompoun		nuuy are				i uic woi	lu	
	\mathbf{C}^{a}	C^{b}	C ^c	C ^d	C ^e	\mathbf{C}^{f}	\mathbf{C}^{g}	C^h	C ⁱ	C^{j}
NA			96.20		160.30		216.70		2,70	868.26
ACY	45.00	76.90	4.30	2.10	9.60		2.50	129.70	4,00	448.19
ACE			0.20		8.40		12.50	48.50	0,80	378.31
FLU	138.00	74.80	6.40	13.40	3.50	5.20	22.60	76.70	22,20	503.59
PHE	150.00	200.30	15.70	76.10	4.50	20.00	76.20	35.20	198,00	257.18
ANT	104.00	14.10	0.50	5.00	0.40	3.30	7.00	49.30	30,00	187.27
FLT	67.00	44.10	5.90	7.40	1.70	4.90	47.80	36.00	36,90	216.79
PYR	58.00	24.60	2.40	6.80	0.90	6.60	31.10	33.60	22,80	188.09
BaA	11.00	2.10	0.05	0.80	1.40	1.10	4.70	28.30	2,00	175.99
CRY	22.00	3.60	0.50	1.50	0.50	3.10*	10.60	26.20	3,60	211.56
BbF	9.00	2.30	0.10	1.10	0.90	1.50	5.80	5.20	2,60	230.15
BaP	25.00	1.60	0.01	0.60	10.30	1.20	3.30	3.00	2,30	159.55
DBA			0.01		2.40	0.10	1.30	7.10	0,30	174.97
IND	5.00	1.20	0.04		0.30	2.50	3.90	5.30	2,70	123.08
BGP		1.10	0.10	4.40	3.70	3.40	5.60	5.60	3,10	219.32
Total PAH	634.00	446.70	132.41	119.20	208.80	52.90	451.60	489.70	334,00	4342.30

Table 3. Comparison of the average total (particulate + gaseous) PAH concentrations (ng/m^3) of each individual compound at the study area and other cities around the world

^a Khalili, 1992 (Chicago, IL USA); ^b Odabasi et al., 1999 (Chicago, IL USA); ^c Poor et al., 2004 (Gandy Bridge, Tampa, FL USA); ^d Halsall et al., 1994 (London, England); ^e Lin et al., 2002 (Tainan, Taiwan); ^f Tsapakis and Stephanou, 2005 (Heraklion, Greece), *: CRY/triphenylene; ^g Tasdemir and Esen, 2007 (Merinos, Bursa, Turkey); ^h Fang et al., 2004c (Tunghai University Campus, Taiwan); ⁱ Li et al., 2006 (Luhu Park, Guangzhou, South China); ^j Present study

	Summer	ſ			Winter			
PAH compounds	Particul	ate phase	Gaseous	phase	Particul	ate phase	Gaseous	phase
	Mean	SD^{a}	Mean	SD	Mean	SD	Mean	SD
NA	4.23	1.05	603.51	110.79	29.09	4.31	1100.00	152.58
$\sum 2$ -ring PAHs ^b	4.23	1.05	603.51	110.79	29.09	4.31	1100.00	152.58
ACY	4.70	1.13	290.81	57.78	32.92	5.11	568.48	82.62
ACE	5.05	1.19	250.92	46.35	38.34	6.13	462.77	69.09
FLU	5.08	1.17	305.93	60.11	35.63	5.45	660.99	96.03
PHE	8.38	1.91	160.95	32.65	48.04	7.35	297.55	42.93
ANT	7.07	1.65	109.84	22.55	37.21	5.98	220.88	32.06
\sum 3-ring PAHs ^c	30.28	7.01	1118.45	218.10	192.14	30.01	2210.67	321.99
FLT	28.45	6.28	52.80	10.37	156.50	21.29	195.39	29.13
PYR	17.92	3.47	50.44	9.43	107.11	15.07	200.84	29.48
BaA	35.79	6.31	27.98	4.95	166.19	24.09	122.12	18.92
CRY	55.59	10.36	16.81	2.66	278.26	38.20	72.27	10.26
\sum 4-ring PAHs ^d	137.75	25.92	148.03	27.22	708.06	98.63	590.62	87.47
BbF	97.01	9.83	4.76	0.75	348.35	42.05	10.19	1.48
BaP	70.74	12.00	4.98	0.77	231.58	32.33	11.99	1.78
DBA	71.22	12.66	2.79	0.50	271.95	37.47	4.08	0.58
∑5-ring PAHs ^e	238.97	34.40	12.53	2.01	851.88	110.10	26.26	3.82
IND	48.39	8.99	2.42	0.49	190.10	24.05	5.28	0.88
BGP	90.85	16.79	2.83	0.50	338.70	42.83	6.22	1.01
\sum 6-ring PAHs ^f	139.24	25.24	5.25	0.98	528.80	66.88	11.50	1.89

Table 4. Atmospheric concentrations (ng/m^3) of the individual PAH compounds and different categories of PAHs based on aromatic ring number in the particulate and gaseous phases during the summer and winter seasons

^aStandard deviation, ^bTotal 2-ring PAH compound, ^cTotal 3-ring PAH compounds, ^dTotal 4-ring PAH compounds, ^eTotal 5-ring PAH compounds, ^fTotal 6-ring PAH compounds

	Particulate phase	Gaseous phase	Total (particulate + gaseous phases)
NA	6.88	1.82	1.86
\sum 2-ring PAHs	6.88	1.82	1.86
ACY	7.00	1.95	2.04
ACE	7.59	1.84	1.96
FLU	7.01	2.16	2.24
PHE	5.73	1.85	2.05
ANT	5.26	2.01	2.22
\sum 3-ring PAHs	6.35	1.98	2.10
FLT	5.50	3.70	4.35
PYR	5.98	3.98	4.52
BaA	4.64	4.36	4.53
CRY	5.01	4.30	4.85
\sum 4-ring PAHs	5.14	3.99	4.56
BbF	3.59	2.14	3.53
BaP	3.27	2.41	3.23
DBA	3.82	1.46	3.73
\sum 5-ring PAHs	3.56	2.10	3.50
IND	3.93	2.18	3.85
BGP	3.73	2.20	3.68
\sum 6-ring PAHs	3.80	2.19	3.74
∑PAHs	4.20	2.10	2.56

Table 5. Winter/summer concentration ratios for the individual PAH compounds and different categories of PAHs based on aromatic ring number in the particulate phase, gaseous phase and total (particulate + gaseous phases)

			1
	Summer	Winter	All period
PHE/ANT	1.19	1.29	1.27
ANT/ANT + PHE	0.46	0.44	0.44
FLT/PYR	1.59	1.46	1.48
FLT/FLT + PYR	0.61	0.59	0.60
BaP/BGP	0.77	0.68	0.70
BaA/CRY	0.64	0.59	0.60
IND/BGP	0.53	0.56	0.55

Table 6. Diagnostic concentration ratios of selected PAH compounds

Summer					Winter				All period				
		Particula	ate PAHs	Gaseous	PAHs	Particula	ate PAHs	Gaseous P	AHs	Particulate	e PAHs	Gaseous P	PAHs
	TEF ^a	Mean	BaP _{equiv}	Mean	BaP _{equiv}	Mean	BaP _{equiv}	Mean	BaP _{equiv}	Mean	BaP _{equiv}	Mean	BaP _{equiv}
		conc.	conc.	conc.	conc.	conc.	conc.	conc.	conc.	conc.	conc.	conc.	conc.
		(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)
NA	0.001	4.23	0.004	603.51	0.604	29.09	0.029	1100.00	1.10	16.67	0.017	851.59	0.852
ACY	0.001	4.70	0.005	290.81	0.291	32.92	0.033	568.48	0.568	18.83	0.019	429.36	0.429
ACE	0.001	5.05	0.005	250.92	0.251	38.34	0.038	462.77	0.463	21.71	0.022	356.60	0.356
FLU	0.001	5.08	0.005	305.93	0.306	35.63	0.036	660.99	0.661	20.37	0.020	483.22	0.483
PHE	0.001	8.38	0.008	160.95	0.161	48.04	0.048	297.55	0.298	28.17	0.028	229.01	0.229
ANT	0.010	7.07	0.071	109.84	1.10	37.21	0.372	220.88	2.21	22.14	0.221	165.13	1.65
FLT	0.001	28.45	0.028	52.80	0.053	156.50	0.157	195.39	0.195	92.50	0.093	124.29	0.124
PYR	0.001	17.92	0.018	50.44	0.050	107.11	0.107	200.84	0.201	62.52	0.063	125.57	0.126
BaA	0.100	35.79	3.579	27.98	2.80	166.19	16.619	122.12	12.21	100.93	10.093	75.06	7.506
CRY	0.010	55.59	0.556	16.81	0.168	278.26	2.783	72.27	0.723	166.91	1.669	44.65	0.446
BbF	0.100	97.01	9.701	4.76	0.476	348.35	34.835	10.19	1.02	222.39	22.239	7.49	0.749
BaP	1.00	70.74	70.74	4.98	4.98	231.58	231.58	11.99	11.99	151.05	151.05	8.50	8.50
DBA	1.00	71.22	71.22	2.79	2.79	271.95	271.95	4.08	4.08	171.53	171.53	3.44	3.44
IND	0.100	48.39	4.839	2.42	0.242	190.10	19.01	5.28	0.528	119.23	11.923	3.85	0.385
BGP	0.010	90.85	0.909	2.83	0.028	338.70	3.387	6.22	0.062	214.79	2.148	4.53	0.045
Total carcinogenicity a	activity (T	CA)	161.688		14.30		580.984		36.309		371.135		25.321
Contribution of BaA to	the TCA	(%)	2.213		19.58		2.86		33.628		2.719		29.64
Contribution of BbF to	the TCA	(%)	5.999		3.33		5.99		2.809		5.992		2.958
Contribution of BaP to	the TCA	(%)	43.751		34.83		39.86		33.022		40.699		33.569
Contribution of DBA t	o the TCA	A (%)	44.047		19.51		46.81		11.237		46.217		13.585
Contribution of IND to	the TCA	(%)	2.993		1.692		3.272		1.454		3.213		1.52

Table 7. BaP equivalent concentrations for PAH compounds in the particulate and gaseous phases during the summer and winter seasons and the period of study

^a TEF values from Nisbet and LaGoy (1992)



Figure 1. Relative contribution of each individual PAH compound and different categories of PAHs based on aromatic ring number to the total concentrations of PAH compounds in the particulate phase, gaseous phase and total (particulate + gaseous phases) during the period of study: (a) individual PAH compounds, and (b) two-to six-ring PAHs



Figure 2. Total (particulate + gaseous) PAH concentrations of each individual compound and different categories of PAHs based on aromatic ring number in the ambient air of the study area during the period of study: (a) individual PAH compounds, and (b) two-to six-ring PAHs



Figure 3. Comparison of the total (particulate + gaseous) PAH concentrations of each individual compound and different categories of PAHs based on aromatic ring number during the summer and winter seasons: (a) individual PAH compounds, and (b) two-to six-ring PAHs



Figure 4. Correlation between the ambiant air temperature and the total PAHs concentrations in the particulate and gaseous phases



Figure 5. Relative contribution of each individual PAH compound and different categories of PAHs based on aromatic ring number to the total concentrations of PAH compounds in the particulate and gaseous phases during the summer season: (a) individual PAH compounds, and (b) two-to six-ring PAHs



Figure 6. Relative contribution of the individual PAH compounds and different categories of PAHs based on aromatic ring number to the total concentrations of the PAH compounds in the particulate and gaseous phases during the winter season: (a) individual PAH compounds, and (b) two-to six-ring PAHs