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Abstract

In this study, three receptor models [factor analysis/multiple linear regression (FA/MLR), positive matrix factorization (PMF) and UNMIX] were applied seasonally to investigate the source apportionment of PAHs in the atmospheric environment of Alexandria, and a lifetime cancer risk was assessed. $\sum_{44}$ (gas + particle) PAH concentrations varied from 330 - 1770 ng/m^3 and 170 - 1290 ng/m^3 in the summer and winter seasons respectively. PAH concentrations at the industrial sites were significantly higher than the traffic and residential sites during the winter season ($p < 0.001$). Summer PAH concentrations were significantly higher than the winter season at the traffic sites ($p = 0.027$). Results obtained from the three receptor models were comparable. Vehicle emissions, both diesel and gasoline contributed on average 36.0-49.0 % and 19.0-34.0 % respectively, natural gas combustion 11.0-27.0 % and, during the summer only, also evaporative/uncombusted petroleum sources 8.00-18.0 %. Seasonal trends were found for the gasoline emission source. Overall, PMF and UNMIX models afforded better source identification than did FA/MLR. The lifetime cancer risk assessment showed that incremental lifetime cancer risks (ILTCRs) were greater than the acceptable level of 10^{-6} through dermal and ingestion routes at all the investigated sites and through the inhalation route at the industrial and traffic sites only. Total ILTCRs (6.64×10^{-3} - 4.42×10^{-2}) were much greater than the range of 10^{-6}, indicating high potential health risk to the local residents.

Keywords

Atmospheric pollution, PAHs, FA/MLR, PMF, UNMIX, lifetime cancer risk

1- Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants in urban atmospheres. Fuel combustion (van Drooge and Ballista, 2009; Chen et al. 2013), waste incineration, wood and cool combustion, power generation plants, and industrial processes such as smelting operations are all considered as major sources of atmospheric PAHs (Mandalakis et al. 2005). Most of these activities are concentrated in the urban centers and thus the exposure of the environment and humans to PAHs is unavoidable.

Due to their persistent, bio-accumulative, carcinogenic and mutagenic properties related to health problems, such as cataracts, kidney and liver damage, and jaundice, PAHs have attracted a significant amount of attention in recent years (Dong and Lee, 2009). Accordingly, air quality standards have been implemented to safeguard human health against the adverse effects of PAHs (WHO, 1987, 2000; Environment Australia, 1999). However, a first step in the air quality evaluation, and eventually improvement of its quality, is the monitoring of the ambient air and the identification of potential emission sources.

To apportion sources, several receptor models have been developed in the past decades. Among them, the two main approaches are multivariate models and chemical mass balance model (CMB) wherein the latter is the method of choice when the impacting sources and their profiles have been predetermined (Sofowote et al. 2008). Three important receptor models, namely factor analysis/multiple linear regression model (FA/MLR) (Simcik et al. 1999; Larsen and Baker, 2003; Liu et al. 2009; Gupta et al. 2011; Shi et al. 2011), Unmix model (Hopke, 2003; Zhang et al. 2012) and positive matrix factorization model (PMF) (Larsen and Baker, 2003; Srivastava et al., 2007; Song et al., 2007; Sofowote et al. 2008; Wang et al. 2009; Ma et al. 2010), have been frequently used and proved to be useful tools in source apportionments studies (Li et al., 2012) without prior knowledge of source profiles or source characteristics (Guo et al. 2004). One advantage of applying PMF and UNMIX is their ability to solve the problem of negative factor loadings/scores by integrating non-negativity constrained factor analysis, making factor loadings and scores more interpretable (Larsen and Baker, 2003).

The release of massive amounts of pollutants in the atmospheric environment of Egypt as a result of the large population, rapid urbanization and industrial expansion, and the increased utilization of fossil fuels in automobiles, trucks and public transportation (EEAA, 2007) has raised serious concern about the potential hazard of these pollutants to the public health. Yet puublished data on the levels of PAHs in the atmospheric environment of Egypt is very limited probably due to the methodological difficulties. Few available studies investigated the levels of aliphatic and aromatic hydrocarbons in particulate fallout (Aboul-Kassim and Simoneit, 1995; Barakat, 2002) and particles emitted during open burning of municipal solid wastes (Barakat, 2003) in Alexandria. One recent study (Nassar et al. 2011) investigated the levels of PAHs and selected nitrated derivatives in total suspended particulates collected from Greater Cairo, Egypt, but a comprehensive survey for emission sources of PAHs for both gas and particle phases in a major Egyptian urban city was not previously performed.

In the current study, atmospheric concentrations of 44 parent and alkylated PAHs in both the gaseous and particulate phases were investigated during the summer and winter seasons in Alexandria, the second largest urban city in Egypt after the capital Cairo. The objectives of this work were to determine the spatial and seasonal variations in the levels of PAHs in both phases, to identify emission sources of PAHs and their contribution levels by means of various methods such as distribution patterns, FA/MLR, PMF and UNMIX receptor models. The study extends to conduct a lifetime cancer risk assessment from the exposure to atmospheric PAHs via inhalation, ingestion and dermal contact.

2- Materials and methods

2.1. Study area and sampling

Detailed information about the study area and sampling were published elsewhere (Khairy and Lohmann, 2012). Alexandria is the second-largest city of Egypt, with a total surface area of 2300 km^2 and a population of 4.5 million, extending about 90 km along the coast of the Mediterranean Sea on the northwestern side of the Nile Delta (Figure 1) (EEAA, 2007; CAMPAS, 2012). It is an important touristic and recreational resort receiving about 2 million tourists every year. January and February are the coolest rainy months, with daily maximum temperatures typically ranging from 12 to 18 °C and minimum temperatures that could reach 5 °C. July and August are the hottest and driest months of the year, with an average daily maximum temperature of 30 °C (EEAA, 2007).

Figure 1

The total length of paved and unpaved roads in Alexandria is 5310 km, and the number of licensed vehicles of all types is 540,000 (CAMPAS, 2012). Accordingly, vehicles per kilometer of road were reported at 95. Private cars represent 68 % of the total licensed cars followed by light and medium duty trucks (15 %), taxis (5 %), motorcycles (5 %), private and public transportation buses (2 %), heavy duty trucks (2 %), and the rest are various vehicle types owned by the governmental sector (~ 3 %). The majority of the buses, light, medium and heavy duty buses are diesel powered vehicles due to the cheap price of diesel compared to gasoline.

Atmospheric samples were collected from 17 sites in the summer (July-August, 2010) and winter (December-January, 2011) seasons (Figure 1) to be representative of the whole study area. Sampling locations were carefully selected to represent possible emission sources of PAHs including residential, traffic and industrial activities (Site and sampling details are given in appendix A, Table A1). Based on the land-use pattern and the demographic characteristics of Alexandria, mixed activities occur at all the sampling locations (Table A1). A traffic-residential mixed pattern indicates that the sample was taken from a main road characterized by heavy traffic density, and surrounded by residential buildings, whereas a residential-traffic indicates that the sample was taken from a side road with high density of residential buildings and lighter traffic density. For simplicity, sampling sites were classified according to the major activity prevailing at each site into traffic, residential and industrial sites (Figure 1). Active sampling was performed using a high volume air sampler (TE-1000 PUF, Tisch Environmental, USA) equipped with quartz fiber filter (GFF, 10 cm diameter) collecting particle-bound compounds and polyurethane foam (10 x 8 cm diameter) retaining compounds in the gaseous phase. Samples were taken at each of the 17 sites for 2-3 days depending on the availability of the power supply (See Table A1 for sampling dates and volumes). A total of 41 GFF and 34 PUF samples were analyzed each season. More details about sampling methodology and preparation of filters and PUFs can be found in Khairy and Lohmann (2012). During the sampling time, the meteorological parameters, including ambient temperature, relative humidity, wind speed/direction, and precipitation, were recorded (Table A1).

2.2. Analytical procedures

GFFs and PUFs were processed separately. Samples were extracted using a Dionex ASE 350 (Dionex Corporation, Sunnyvale, CA 94088) accelerated solvent extraction device after spiking with the surrogate standard mixture (acenaphthylene-d_8, anthracene-d_{10}, chrysene-d_{12} and perylene-d_{12}). Methods used for the extraction of the GFFs and PUFs are described in Lambert et al. (2011) and Khairy and Lohmann (2012) respectively. Extracts were concentrated to a final volume of ~1 mL using a rotary evaporator (after solvent exchange into hexane) and passed on a glass chromatographic cleanup column packed with silica gel/alumina (2:1, w/w) in order to remove the interfering compounds.

PAHs were eluted with *n*-hexane/DCM solvent mixture (1:1, v/v) and the collected fraction was concentrated to a final volume of ~ 50 µL. Finally, d_{14}-terphenyl was added as the injection standard before analysis.

Forty four alkylated and parent PAHs (Table A2) were analyzed with an Agilent 6890 Series GC System connected to an Agilent 5973 Network Mass Selective Detector. Separation of PAHs was accomplished with a DB-5 MS fused silica capillary column (30 m×0.25 mm i.d., 0.25 µm film thickness, J&W Scientific). Samples (1 µL) were auto injected in splitless mode with the injection port at 275°C. The MS was operated in EI^+ mode with selected ion monitoring. Method details are described in Khairy and Lohmann (2012). Abbreviations used for the investigated PAHs are shown in Table (A2). Overall, the analysis included procedural blanks, field blanks and matrix spikes, which were carried throughout the entire analytical procedure in a manner identical to the samples. More details about the quality assurance/quality control are provided in the supplementary materials of this work (Text A1 and Table A2).

2.3. Source apportionment techniques

2.3.1. Factor analysis/multiple linear regression (FA/MLR)

In the present study, factor analysis was applied to the measured concentrations of PAHs in Alexandria, Egypt during the summer and winter seasons separately. The total PAH concentrations (gaseous + particulate phases) were used to eliminate the effects of partitioning between phases (Lee et al. 2004). The data matrix contained 34 samples and 28 variables (measured individual PAHs) for each season.

Multiple linear regression analysis was performed on the extracted principle component scores (representing possible sources of PAHs) in order to obtain mass apportionment of the identified sources to the ∑PAH concentration in each sample. More details about the procedures followed in the FA/MLR analysis are provided in the supplementary materials (Text A2). FA and MLR were performed using SPSS statistical software packages (SPSS 13.0).

2.3.2. Positive matrix factorization (PMF)

PMF is a useful factorization method that can calculate source profile and contribution. The principle idea of the PMF is to decompose a matrix of speciated sample data into two matrices—factor contributions and factor profiles. A speciated data set can be viewed as a data matrix X of i by j dimensions, in which i number of samples and j chemical species were measured. The goal of PMF is to identify a number of factors p, the species profile f of each source, and the amount of mass *g* contributed by each factor to each individual sample:

$$X_{ij}=\sum_{k=1}^{p} g_{ik}f_{kj}+e_{ij} \quad (1)$$

where e_{ij} is the residual for each sample/species. PMF allows each data point to be individually weighed. This feature allows the analyst to adjust the influence of each data point, depending on the confidence in the measurement. PMF uses the residual matrix elements (e_{ij}) along with uncertainty estimates (U_{ij}), which is provided by the user to calculate a minimum Q value using a weighed least square method defined as:

$$Q=\sum_{i=1}^{n}\sum_{j=1}^{m}\frac{X_{ij}-\sum_{k=1}^{p}g_{ik}f_{kj}}{U_{ij}} \quad (2)$$

The uncertainty file prepared for the current analysis included the calculated LODs and the recovery standard deviation of the surrogate standards (Larsen and Baker, 2003). The robust Q value reduces the impact of outliers in the fitting of the model. The theoretical Q value should be approximately equal to the number of data entries in the concentration file for a model. The task of PMF model is to minimize this function. More details about PMF can be found in Paatero (2007). The US EPA version of PMF (PMF v3.0.2.2) was used in the present study.

2.3.3. Unmix model

Unmix model is a new type of receptor model based on factor analysis (Hopke 2003). UNMIX was developed to address the shortcomings of both PCA and CMBs (Larsen and Baker 2003). The algorithm of Unmix is to find edges in sets of points in N-dimensional space (Henry, 2003). For a dataset with n samples and m chemical species, the Unmix can reduce the source profiles by projecting the dataset to a plane perpendicular to the first axis of N-dimensional space, and the edges of the projected data represent the samples that identify the sources (Larsen and Baker 2003). For more details, please refer to the EPA UNMIX 6 fundamentals and userguide (US EPA 2007). In this work, EPA Unmix 6.0 model was used.

2.4. Cancer health risk assessment

In the current study, individual PAH potency equivalency factors (PEF) relative to BaP as developed by Collins et al. (1998) were used to estimate multi-component PAH exposure (Table A3). PEFs for the 18 target PAHs were obtained from Nisbet and LaGoy (1992) and Chiang et al. (2009). Exposure is expressed in terms of a lifetime average daily dose (LADD) and is calculated separately for each element and for each exposure pathway according to the USEPA framework (USEPA, 1989, 2004, 2009). Mathematical models used for the calculations of LADD are given in Table (A4, Eqs A1-A3). Exposure parameter values used in the current study are listed in Table (A5). The incremental lifetime cancer risk (ILTCR) was then estimated as the incremental probability of an individual developing cancer over a lifetime as a result of exposure to a potential carcinogen through inhalation, ingestion and dermal contact (Table A4, Eq. A4) The cancer slope factors (CSFs) for BaP used in the present study for the dermal (Chiang et al. 2009), inhalation and ingestion (OEHHA, 2005) exposure routes were 30.5, 3.9 and 12 mg/kg/d respectively. Cancer risks from various exposure routes are assumed to be additive, as long as the risks are for the same individuals and time period. The total incremental lifetime cancer risk (TILCR) was calculated by summing the risks associated with each exposure route (Table A4. Eq. A5). The lower end of the range of acceptable risk distribution (TILCR) is defined by a single constraint on the 95th percentile of risk distribution that must be equal or lower than 10^{-6} for carcinogens (USEPA, 2004, Chiang et al. 2009).

3- Results and discussion

3.1. Atmospheric concentrations of PAHs

A statistical summary of the obtained PAH concentrations in the gas and particle phases during both seasons are given in Tables (A6 and A7). Total (gas + particle) PAH concentrations varied from 330 - 1770 ng/m^3 in the summer season and from 170 - 1290 ng/m^3 in the winter season with average concentrations of 740 $\pm$ 365 and 530 $\pm$ 260 ng/m^3 respectively. Average PAH concentrations were higher than that measured in Chicago, USA ($\sum_{26}$ PAHs = 167 $\pm$ 164 ng/m^3, Simcik et al. 1999), Harbin, China ($\sum_{16}$ PAHs = 100 $\pm$ 94.0 ng/m^3, Ma et al. 2010), Guangzhou, China ($\sum_{16}$ PAHs = 340 $\pm$ 140 ng/m^3, Li et al. 2006), Seoul. Korea ($\sum_{16}$ PAHs = 89.3 $\pm$ 74.3 ng/m^3, Park et al. 2002), Athens, Greece ($\sum_{14}$ PAHs = 28.4 $\pm$ 1.63 ng/m^3, Vasilakos et al. 2007), Bursa, Turkey during the non-heating season ($\sum_{14}$ PAHs = 150 ng/m^3, Esen et al. 2008) and Flanders, Belgium ($\sum_{16}$ PAHs: 57.8 $\pm$ 43.0 ng/m^3, Ravindra et al. 2006), but lower than those measured at Bursa, Turkey during the heating seasons ($\sum_{14}$ PAHs = 1200 ng/m^3. Esen et al. 2008) and in Giza, Egypt ($\sum_{14}$ PAHs = 4300 ng/m^3, Hassan and Khoder, 2011). All the above given PAH concentrations represent the sum of the gas phase and particulate phase.

Gas phase PAH concentrations ranged from 300 - 1400 ng/m^3 in the summer season and from 155 - 870 ng/m^3 in the winter season with average concentrations of 620 $\pm$ 295 ng/m^3 and 380 $\pm$ 170 ng/m^3 respectively. Average concentrations at the industrial (845 ng/m^3) and the traffic sites (640 ng/m^3) were slightly higher than at the residential sites (460 ng/m^3) during the summer season (Figure 2a). In the winter season, PAH concentrations at the industrial sites (average = 680 ng/m^3) were significantly higher than concentrations at the residential (average = 270 ng/m^3) and the traffic sites (average = 365 ng/m^3) (1-way ANOVA, F = 7.602, at $\alpha = 0.05$, $p = 0.006$). In both seasons, all the gas phase samples were dominated by 2-3 rings PAHs (parent and alkylated) comprising > 90 % of the total detected concentrations (Khairy and Lohmann, 2012). 4-rings PAHs had a minor contribution (< 11 %) in all the investigated samples. The most abundant PAHs were C_1-Phn/Ant (6.50-34.0 %), Phn (3.70-28.0 %), and C_2-Phn/Ant (4.30-19.4 %) (Figure A1).

Figure 2

Concentrations of PAHs in the particle phase ranged from 27.0 - 340 ng/m^3 in the summer season and from 14.0 - 420 ng/m^3 in the winter season with average concentrations of 120 ± 79.0 and 147 ± 100 ng/m^3 respectively. In the summer and winter samples, PAH concentrations were significantly higher at the industrial sites (Figure 2b) compared to the traffic and the residential sites (1-way ANOVA, $F_{summer} = 10.6$, $p = 0.002$; $F_{winter} = 26.3$, $p < 0.001$). In contrast to the gas phase PAHs, higher molecular weight PAHs (4, 5 and 6 rings PAHs) and alkylated phenanthrenes predominated in the particle phase (Figure A2).

3.2. Temporal variations in PAH concentrations and Meteorological conditions

Figure (2) shows the variations of the gas phase (a) and particulate (b) PAH concentrations during the summer and winter seasons. Concentrations of the gas phase PAHs were significantly higher in the summer (average temperature: 28 $^\circ$C) compared to the winter season (average temperature: 18 $^\circ$C) ($p = 0.003$). This is different from the northern Chinese cities (Ma et al. 2010) with higher PAH concentrations during the heating season (winter) as a result of increased combustion of fossil fuels. In Alexandria, centralized heating systems do not exist and heating of indoor places depends mainly on electric heaters. In contrast to the gas phase PAHs, no statistical significant difference was observed between the summer and winter concentrations of the particle phase PAHs ($p = 0.352$). To investigate the influence of meteorological conditions on the temporal variations in PAH concentrations, recorded temperatures and wind speed at the sampling sites (Table A1) were correlated against gas and particle phase PAH concentrations. As shown in Table (1), gas phase PAH concentrations increased with temperature. In the summer season, there was a marked increase in the enrichment of the gas phase samples with Phn (17 %) and C_1- Phn/Ant (17 %) which could be related to the increase in the evaporative emissions from petroleum products such as asphalt and coal tar sealant (Massei et al., 2005) as a result of the higher temperatures. Gas phase PAHs were also found to decrease with increasing wind speed ($r = -0.46$, $P < 0.01$, $n = 34$). Higher wind speed in the winter season could increase the pollutant dispersion in the atmosphere. Particulate PAH concentrations showed a weak negative correlation with temperature ($r = -0.15$, $P < 0.01$, $n = 34$). A similar finding was observed in Guiyang, Southwest China (Hu et al. 2012) ($r = -0.17$, $P < 0.05$, $n = 180$). In Alexandria, particulate PAH concentrations were relatively higher in the winter season (Figure 2b) but this difference was statistically insignificant. Based on the strength of the calculated correlation coefficients (moderate to low) in Table (1), we conclude that the temporal variations in the gas phase and particulate PAH concentrations are partially influenced by meteorological conditions, and that the observed temporal variation is mainly attributed to the emission sources. In Alexandria, it is expected that vehicular emissions are the major source of atmospheric PAHs (Barakat, 2002; EEAA, 2011). Although unleaded petrol has recently been used, leaded gasoline is still in use, especially in old vehicles. At the same time, catalytic converters have not yet been extensively introduced to Egypt (EEAA, 2011). The higher PAH concentrations observed during the summer season could be attributed to the marked increase in the traffic density (mainly with gasoline powered vehicles) as a result of the increased number of visitors for recreational purposes (Khairy and Lohmann, 2012). This causes serious congestions on the busy narrow streets as a result of Alexandria's inadequate road networking (Barakat, 2002). Ravindra et al. (2008) indicated that urban areas with congested traffic conditions with vehicles often only traveling short journeys promote the emission of PAHs.

In Alexandria, 40-50 % of the total airborne atmospheric particulates are emitted from diesel engine powered vehicles (EEAA, 2011). Most of the buses and vehicles used in the public transportation, the medium and heavy duty trucks (at the industrial sites) are powered with diesel engines, with an almost equal level of activity during both seasons, which could possibly explain the observed insignificant seasonal variations in the particle phase PAH concentrations.

Table 1

3.2 Source apportionment of PAHs

3.2.1. Factor analysis and multiple linear regression

The rotated factors of atmospheric PAHs in Alexandria during the summer and winter seasons are presented in Tables (A8 and A9) respectively. In the summer season, four factors were extracted explaining 84.3 % of the total variability in the PAH data. The first factor (Factor 1) accounted for 41.1 % of the total variance and was highly loaded on alkylated phenanthrenes and dibenzothiophenes, BeP, BaP, BbF, BkF, InP Flra and Pyr, which were previously used as tracers for diesel emissions (Li and Khamens, 1993; Larsen and Baker, 2003; Li et al. 2003; Sofowote et al. 2008; Chen et al. 2013). C_1-Phn/Ant was used as the tracer for this factor (for the multiple regression analysis).

Factor 2 accounted for 22.8 % of the total variance and was highly loaded on BghiP, Acy, Phn, Ace, DibA and Flr. This factor was also moderately loaded on Biph, Per and Ant. Phn and BghiP have been used as indicators of vehicle emissions from gasoline powered vehicles (Harrison et al. 1996; Ho et al. 2009). Thus this factor was selected to represent gasoline emissions and BghiP was used as the tracer for this factor.

Factor 3 accounted for 14.6 % of the total variance and was highly loaded on Chry, BaA which were previously used as indicators of natural gas combustion (Rogge et al., 1993; Ravindra et al. 2008). Natural gas is used in Alexandria in home appliances and as an alternate source of fuel in vehicles (EEAA, 2011). Chry was selected as the tracer of this source factor. Factor 4 accounted for 5.70 % of the total variance and was moderately loaded on Nap, Biph and Flr (Table A8). This pattern of the predominance of the low molecular weight PAHs could be related to the ground evaporation during the summer (hot) season and/or the unburned fuel. Factor 4 was assigned to represent the evaporative/unburned petroleum source and the tracer was Nap.

In the winter season, four factors were extracted explaining 86.0 % of the total variability in the PAH data. The first three factors representing diesel emissions (BaP was the tracer), natural gas combustion (Chry was the tracer) and gasoline emissions (Pyr was the tracer) were quite similar to those extracted in the summer season (Tables A8 and A9), and accounted for 26.0 %, 23.7 % and 19.4 % respectively of the total variability in the data. Factor 4 did not show its signal in the summer season. It accounted for 16.7 % of the total variability and was heavily loaded on Ret, Flr, Nap, Ace and DBT (Table SI 9). Ret was previously used as a representative of wood combustion (Simcik et al. 1999 and references therein).

3.2.3. Positive matrix factorization (PMF)

In this work, a 34 x 28 (34 samples and 28 PAH species) dataset was introduced into the EPA PMF 3.0 model to estimate the source contributions to PAHs. Ambient concentrations of PAHs (gas + particle) in Alexandria during the summer and winter seasons were entered separately as raw data in the PMF model. The uncertainty file prepared for the current analysis included the calculated LODs and the recovery standard deviation of the surrogate standards (Larsen and Baker, 2003). For each data set the number of factors was varied, each time running the model several times starting from a different initial seed. This was done to better understand the stability of the solution. The model was run in the robust mode to keep outliers from unduly influencing the results. The ‘‘optimal’’ solution (i.e. number of factors) was considered to have a Q value near the theoretical Q value and a solution that did not depend on the initial seed. Four source factors were extracted in the summer season and 3 source factors were extracted in the winter season. Profiles obtained from the PMF model are presented in Figure (3)

Figure 3

In the summer season, factor 1 accounted for 16.0 % of the sum of the measured PAHs and had good similarities to natural gas emissions. In natural gas combustion, Chry, BaA, Flra, Pyr are expected to be present with low contribution of the high molecular weight PAHs (Simcik et al. 1999; Lee et al. 2004; Ma et al. 2010), as seen in this factor (Figure 3a).

Factor 2 explained 17.0 % of the sum of the measured PAHs and was dominated by methyl phenanthrenes and the 2-3 rings PAHs (Figure 3b). This factor contained the more volatile PAHs and appeared only in the summer (warm) season as expected by temperature driven process. Additionally, this factor is also consistent with the evaporation of uncombusted petroleum during fuel handling and refueling operations based on its high loading of methyl phenanthrenes (Lee et al. 2004). Accordingly, this factor was selected to represent the evaporative/uncombusted petroleum source.

Factors 3 (Figure 3c) and 4 (Figure 3d) accounted for 37.0 % and 30.0 % respectively of the sum of the measured PAHs and were consistent with vehicle emissions. The profiles of both factors showed some similarities with the dominance of Phn, Flra, Pyr, methyl phenanthrenes, and a significant contribution from the 5 and 6 rings PAHs (BbF, BkF, BeP, BaP, InP and BghiP). Concentrations of Phn, Flra, Pyr, Inp and the 5-rings PAHs were higher in the profile of factor 3 (Figure 3c), which is consistent with the source of diesel engine emissions (Wang et al. 2009). Additionally, InP was more enriched in diesel emissions (Li and Khamens; Simcik et al. 1999; Li et al. 2003). The profile of factor 4 (Figure 3d) had more contribution from BghiP, which has been previously used as a tracer of gasoline emissions (Simcik et a. 1999; Li et al. 2003; Wang et al. 2009; Chen et al. 2013), and less contribution from the 5-rings PAHs compared to the profile of factor 3. Accordingly, Factors 3 and 4 were selected to represent diesel and gasoline emissions respectively.

In the winter season, 3 source factors (Figure 3) were extracted from the PMF model namely gasoline emissions (Factor 1), diesel emissions (Factor 2) and natural gas combustion (Factor 3), each representing 24.9 %, 48.5 %and 26.6 % respectively of the ∑PAHs. Source profiles representing diesel emissions, gasoline emissions and natural gas combustion were similar to those obtained from the summer season with minor variations. Estimated average contribution of the extracted sources in both seasons is shown in Figure (A3).

3.2.4. Unmix model

Four factors during the summer season and three factors during the winter season were extracted by the UNMIX model representing the source profiles, and showed similar results to the PMF model (Figure 3). Factor 1 represented natural gas combustion source (Figure 3e), Factor 2 might be identified as the evaporative/uncombusted petroleum, which appeared in the summer season only (Figure 3f), Factor 3 represented diesel emission source (Figure 3g), and Factor 4 represented gasoline emission source (Figure 3h). The estimated average contribution for the extracted sources in the summer and winter seasons was also similar to PMF model (Figure A3).

3.2.5. Comparison between the mean source contributions and the predictive ability of the FA/MLR, PMF and UNMIX models

The three factor analysis techniques were found to be very useful in quantifying source contributions and identifying the chemical profiles of sources without any prior knowledge of the number or types of sources impacting the atmospheric environment of Alexandria. PMF and UNMIX models extracted the same number of sources in the summer and winter seasons, with similar source profiles (Figure 3) and average source contribution (Figure A3). FA/MLR model extracted a source factor representing wood combustion that was not identified by the PMF and UNMIX models. This could arise from the higher degree of uncertainty associated with the identification of sources with FA/MLR as there is no scaling of data based on uncertainty estimates before analysis (Larsen and Baker, 2003) (See text A3 in the supplementary materials for more details).

As shown in Figure (A4), good correlations were found between the predicted PAH concentrations obtained by the three models and the measured PAHs concentration, with $R^2 \geq 0.95$ for both the summer and winter seasons, indicating their strong effectiveness.

3.2.6. Distribution of PAH source contributions

As shown in the estimated average contribution of the extracted sources from the three models (Figure A3), vehicle emissions (diesel + gasoline) were the major source of PAHs to the atmospheric environment of Alexandria with an average contribution of 69.0 % - 71.0 % in the winter and summer seasons respectively. In both seasons, diesel emissions were the dominant source, as was indicated in previous studies (Barakat, 2002; Khairy and Lohmann, 2012). Estimated average contributions (ng/m^3) for each source category at the sampling sites using the output of the PMF model are shown in Figure (4). In both seasons, diesel emissions made the largest contribution for PAHs at the industrial sites (Figure 4a), which accounted for an average of 65.0 % of the total measured PAHs concentrations. This is consistent with the higher density of the medium and heavy duty trucks powered by diesel engines that can be observed at the industrial sites. Estimated PAH concentrations that originated from diesel emissions were lower at the traffic and residential sites. However, at 4 of the traffic sites (T2, T3, T8 and T9), and two residential sites (R1, R2), relatively higher diesel emission contributions were observed compared to the other sites. These sites are characterized by higher densities of public transportation buses and medium duty trucks (T2, T3) that are powered by diesel engines compared to the other sites. Diesel emissions accounted for 43.0% and 35.0 % of the total measured PAH concentrations at the traffic and residential sites respectively. Estimated PAH concentrations from the gasoline emission source were higher at the traffic sites (Figure 4b), followed by the residential and industrial sites and accounted for 49.0 %, 38.0 % and 22.0 % respectively of the total measured PAH concentrations. Relatively high % contributions from the diesel and gasoline emissions were observed at the residential sites during the summer season. One explanation for that is the that most of the residential sites examined in the current work were either close to a main road with high traffic activity, and/or located in a narrow road with serious congestions (observed during the sampling campaign) enhancing the emission of PAHs (Ravinda et al. 2008).

Estimated PAH concentrations from the natural gas combustion source, which showed less contribution compared to the other two sources, were higher at the residential sites, followed by the industrial sites (detected at only one site, In2) and the traffic sites, and accounted for 27.0 %, 13.0 % and 9.00 % respectively of the total PAH concentrations. These findings seem reasonable as the natural gas is used as the energy source in home appliances and in industrial plants (EEAA, 2011).

Figure 4

No seasonal trends were observed for the estimated PAH concentrations from the diesel emissions and the natural gas combustion emission sources at all the sites in Alexandria (Figure 4a,c). However, estimated PAH concentrations from the gasoline emissions were significantly higher in the summer season at the traffic (P = 0.027) and residential sites (P = 0.015) (Figure 4b), which is attributed to the higher traffic density during the summer season as a result of the increased number of visitors for recreational purposes (Khairy and Lohmann, 2012). Overall, obtained source distributions were closely related to the human activities around the sampling sites (Khairy and Lohmann 2012).

3.3. Cancer risk assessment from the exposure to atmospheric PAHs

The aim of this risk assessment was to investigate the possibility of cancer development among the local residence in Alexandria as a result of exposure to the atmospheric PAH concentrations via inhalation, ingestion and dermal exposure routes. The geometric means of the summer and winter concentrations of each of the 18 investigated individual PAHs were used for the further calculations in the risk assessment study.

Estimates of the lifetime average daily dose (LADD) and the incremental lifetime cancer risks (ILTCR) for the inhalation, ingestion and dermal exposure routes are given in Tables (A12, A13 and A14) respectively. Greater possibility of occurrence of adverse health effects were associated with the dermal ($ILTCR_{der}$) contact to atmospheric PAHs (6.48×10^{-3} - 4.41×10^{-2}), followed by the ingestion exposure route ($ILTCR_{ing}$) (1.31×10^{-5} - 8.92×10^{-5}), and finally the inhalation exposure route ($ILTCR_{inh)}$ (1.08×10^{-6} - 5.88×10^{-6}). Calculated total incremental lifetime cancer risks (TILTCR) are shown in Figure (5). All the calculated values at all the sites were higher than 10^{-3}, which greatly exceed the USEPA acceptable level of 10^{-6} (USEPA, 2004) indicating high potential carcinogenic health risk. It was obvious that the dermal contact exposure route was the major contributor to the total lifetime cancer risk comprising > 99 % of the calculated values of TILTCR at all the investigated sites. Concerning the individual toxicity of the target PAHs, the compounds that contributed most to the total estimated risk were BbF (81.3–94.0 %) and BaP (5.00-12.5 %), which were associated with vehicular emissions (Figure 3). We therefore conclude that the cancer risk associated with the exposure to PAHs emitted from vehicle emissions is not negligible and should be taken into account for health protection in the future.

Figure 5

4. Conclusions

Urban cities are large sources of atmospheric pollution. Understanding the seasonal variability in the sources of atmospheric PAHs requires the existence of emission inventories, which in terms will help to develop efficient pollution control strategies and assist in the protection of the human health. Our results indicted that the atmospheric environment of Alexandria, Egypt is highly polluted with PAHs, with concentrations much higher that in other urban cities worldwide. The spatial distribution of PAHs, temporal variations and source apportionment results indicated that vehicle emissions, especially from diesel powered engines are the major source of PAHs in Alexandria. Although the three receptor models gave comparable results with good matching between the predicted and measured PAH concentrations, PMF and UNMIX models are more reliable and accurate than the FA/MLR model which is associated with a higher degree of uncertainty because of the independence of the calculations on the quality assurance data and the negative loadings constrains. Based on our findings, at least two receptor models should be used to confirm the output of the source apportionment. Our results also indicated that there is a high potential risk of cancer development as a result of the exposure to PAHs via inhalation, ingestion and dermal contact and that PAH exposures is not negligible and should be taken into account for health protection in the future.

Appendix. Supplementary data

5. References

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