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Source Apportionment and Risk Assessment of Polycyclic Aromatic Hydrocarbons in the Atmospheric Environment of Alexandria, Egypt

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1 **Source Apportionment and Risk Assessment of Polycyclic Aromatic Hydrocarbons**
2 **in the Atmospheric Environment of Alexandria, Egypt**

3
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14
15
16 **Abstract**

17
18 In this study, three receptor models [factor analysis/multiple linear regression (FA/MLR),
19 positive matrix factorization (PMF) and UNMIX] were applied seasonally to investigate
20 the source apportionment of PAHs in the atmospheric environment of Alexandria, and a
21 lifetime cancer risk was assessed. \sum_{44} (gas + particle) PAH concentrations varied from
22 330 - 1770 ng/m³ and 170 - 1290 ng/m³ in the summer and winter seasons respectively.
23 PAH concentrations at the industrial sites were significantly higher than the traffic and
24 residential sites during the winter season ($p < 0.001$). Summer PAH concentrations were
25 significantly higher than the winter season at the traffic sites ($p = 0.027$). Results obtained
26 from the three receptor models were comparable. Vehicle emissions, both diesel and
27 gasoline contributed on average 36.0-49.0 % and 19.0-34.0 % respectively, natural gas
28 combustion 11.0-27.0 % and, during the summer only, also evaporative/uncombusted
29 petroleum sources 8.00-18.0 %. Seasonal trends were found for the gasoline emission
30 source. Overall, PMF and UNMIX models afforded better source identification than did
31 FA/MLR. The lifetime cancer risk assessment showed that incremental lifetime cancer
32 risks (ILTCRs) were greater than the acceptable level of 10^{-6} through dermal and

33 ingestion routes at all the investigated sites and through the inhalation route at the
34 industrial and traffic sites only. Total ILTCRs (6.64×10^{-3} - 4.42×10^{-2}) were much greater
35 than the range of 10^{-6} , indicating high potential health risk to the local residents.

36 **Keywords**

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

38

39

40 **1- Introduction**

41

42

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

49 Due to their persistent, bio-accumulative, carcinogenic and mutagenic properties related
50 to health problems, such as cataracts, kidney and liver damage, and jaundice, PAHs have
51 attracted a significant amount of attention in recent years (Dong and Lee, 2009).

52 Accordingly, air quality standards have been implemented to safeguard human health
53 against the adverse effects of PAHs (WHO, 1987, 2000; Environment Australia, 1999).

54 However, a first step in the air quality evaluation, and eventually improvement of its
55 quality, is the monitoring of the ambient air and the identification of potential emission
56 sources.

57

58 To apportion sources, several receptor models have been developed in the past decades.
59 Among them, the two main approaches are multivariate models and chemical mass
60 balance model (CMB) wherein the latter is the method of choice when the impacting
61 sources and their profiles have been predetermined (Sofowote et al. 2008). Three
62 important receptor models, namely factor analysis/multiple linear regression model
63 (FA/MLR) (Simcik et al. 1999; Larsen and Baker, 2003; Liu et al. 2009; Gupta et al.
64 2011; Shi et al. 2011), Unmix model (Hopke, 2003; Zhang et al. 2012) and positive
65 matrix factorization model (PMF) (Larsen and Baker, 2003; Srivastava et al., 2007; Song
66 et al., 2007; Sofowote et al. 2008; Wang et al. 2009; Ma et al. 2010), have been
67 frequently used and proved to be useful tools in source apportionments studies (Li et al.,
68 2012) without prior knowledge of source profiles or source characteristics (Guo et al.
69 2004). One advantage of applying PMF and UNMIX is their ability to solve the problem
70 of negative factor loadings/scores by integrating non-negativity constrained factor
71 analysis, making factor loadings and scores more interpretable (Larsen and Baker, 2003).

72

73 The release of massive amounts of pollutants in the atmospheric environment of Egypt as
74 a result of the large population, rapid urbanization and industrial expansion, and the
75 increased utilization of fossil fuels in automobiles, trucks and public transportation
76 (EEAA, 2007) has raised serious concern about the potential hazard of these pollutants to
77 the public health. Yet published data on the levels of PAHs in the atmospheric
78 environment of Egypt is very limited probably due to the methodological difficulties.
79 Few available studies investigated the levels of aliphatic and aromatic hydrocarbons in
80 particulate fallout (Aboul-Kassim and Simoneit, 1995; Barakat, 2002) and particles

81 emitted during open burning of municipal solid wastes (Barakat, 2003) in Alexandria.
82 One recent study (Nassar et al. 2011) investigated the levels of PAHs and selected
83 nitrated derivatives in total suspended particulates collected from Greater Cairo, Egypt,
84 but a comprehensive survey for emission sources of PAHs for both gas and particle
85 phases in a major Egyptian urban city was not previously performed.

86

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

95

96 **2- Materials and methods**

97

98 **2.1. Study area and sampling**

99

100 Detailed information about the study area and sampling were published elsewhere
101 (Khairy and Lohmann, 2012). Alexandria is the second-largest city of Egypt, with a total
102 surface area of 2300 km² and a population of 4.5 million, extending about 90 km along
103 the coast of the Mediterranean Sea on the northwestern side of the Nile Delta (Figure 1)
104 (EEAA, 2007; CAMPAS, 2012). It is an important touristic and recreational resort
105 receiving about 2 million tourists every year. January and February are the coolest rainy

106 months, with daily maximum temperatures typically ranging from 12 to 18 °C and
107 minimum temperatures that could reach 5 °C. July and August are the hottest and driest
108 months of the year, with an average daily maximum temperature of 30 °C (EEAA, 2007).

109
110
111

Figure 1

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

120

121 Atmospheric samples were collected from 17 sites in the summer (July-August, 2010)
122 and winter (December-January, 2011) seasons (Figure 1) to be representative of the
123 whole study area. Sampling locations were carefully selected to represent possible
124 emission sources of PAHs including residential, traffic and industrial activities (Site and
125 sampling details are given in appendix A, Table A1). Based on the land-use pattern and
126 the demographic characteristics of Alexandria, mixed activities occur at all the sampling
127 locations (Table A1). A traffic-residential mixed pattern indicates that the sample was
128 taken from a main road characterized by heavy traffic density, and surrounded by
129 residential buildings, whereas a residential-traffic indicates that the sample was taken
130 from a side road with high density of residential buildings and lighter traffic density. For

131 simplicity, sampling sites were classified according to the major activity prevailing at
132 each site into traffic, residential and industrial sites (Figure 1). Active sampling was
133 performed using a high volume air sampler (TE-1000 PUF, Tisch Environmental, USA)
134 equipped with quartz fiber filter (GFF, 10 cm diameter) collecting particle-bound
135 compounds and polyurethane foam (10 x 8 cm diameter) retaining compounds in the
136 gaseous phase. Samples were taken at each of the 17 sites for 2-3 days depending on the
137 availability of the power supply (See Table A1 for sampling dates and volumes). A total
138 of 41 GFF and 34 PUF samples were analyzed each season. More details about sampling
139 methodology and preparation of filters and PUFs can be found in Khairy and Lohmann
140 (2012). During the sampling time, the meteorological parameters, including ambient
141 temperature, relative humidity, wind speed/direction, and precipitation, were recorded
142 (Table A1).

143

144 **2.2. Analytical procedures**

145

146 GFFs and PUFs were processed separately. Samples were extracted using a Dionex ASE
147 350 (Dionex Corporation, Sunnyvale, CA 94088) accelerated solvent extraction device
148 after spiking with the surrogate standard mixture (acenaphthylene-d₈, anthracene-d₁₀,
149 chrysene-d₁₂ and perylene-d₁₂). Methods used for the extraction of the GFFs and PUFs
150 are described in Lambert et al. (2011) and Khairy and Lohmann (2012) respectively.
151 Extracts were concentrated to a final volume of ~1 mL using a rotary evaporator (after
152 solvent exchange into hexane) and passed on a glass chromatographic cleanup column
153 packed with silica gel/alumina (2:1, w/w) in order to remove the interfering compounds.

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

157

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

169

170 **2.3. Source apportionment techniques**

171 **2.3.1. Factor analysis/multiple linear regression (FA/MLR)**

172 In the present study, factor analysis was applied to the measured concentrations of PAHs
173 in Alexandria, Egypt during the summer and winter seasons separately. The total PAH
174 concentrations (gaseous + particulate phases) were used to eliminate the effects of
175 partitioning between phases (Lee et al. 2004). The data matrix contained 34 samples and
176 28 variables (measured individual PAHs) for each season.

177 Multiple linear regression analysis was performed on the extracted principle component
178 scores (representing possible sources of PAHs) in order to obtain mass apportionment of
179 the identified sources to the \sum PAH concentration in each sample. More details about the
180 procedures followed in the FA/MLR analysis are provided in the supplementary materials
181 (Text A2). FA and MLR were performed using SPSS statistical software packages (SPSS
182 13.0).

183

184 **2.3.2. Positive matrix factorization (PMF)**

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

192

$$193 \quad X_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (1)$$

194

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

200

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

201

202

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

210

211 **2.3.3. Unmix model**

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

221

222 **2.4. Cancer health risk assessment**

223 In the current study, individual PAH potency equivalency factors (PEF) relative to BaP as
224 developed by Collins et al. (1998) were used to estimate multi-component PAH exposure
225 (Table A3). PEFs for the 18 target PAHs were obtained from Nisbet and LaGoy (1992)
226 and Chiang et al. (2009). Exposure is expressed in terms of a lifetime average daily dose
227 (LADD) and is calculated separately for each element and for each exposure pathway
228 according to the USEPA framework (USEPA, 1989, 2004, 2009). Mathematical models
229 used for the calculations of LADD are given in Table (A4, Eqs A1-A3). Exposure
230 parameter values used in the current study are listed in Table (A5). The incremental
231 lifetime cancer risk (ILTCR) was then estimated as the incremental probability of an
232 individual developing cancer over a lifetime as a result of exposure to a potential
233 carcinogen through inhalation, ingestion and dermal contact (Table A4, Eq. A4) The
234 cancer slope factors (CSFs) for BaP used in the present study for the dermal (Chiang et
235 al. 2009), inhalation and ingestion (OEHHA, 2005) exposure routes were 30.5, 3.9 and
236 12 mg/kg/d respectively. Cancer risks from various exposure routes are assumed to be
237 additive, as long as the risks are for the same individuals and time period. The total
238 incremental lifetime cancer risk (TILCR) was calculated by summing the risks associated
239 with each exposure route (Table A4. Eq. A5). The lower end of the range of acceptable
240 risk distribution (TILCR) is defined by a single constraint on the 95th percentile of risk
241 distribution that must be equal or lower than 10^{-6} for carcinogens (USEPA, 2004, Chiang
242 et al. 2009).

243

244

245

246 3- Results and discussion

247 3.1. Atmospheric concentrations of PAHs

248 A statistical summary of the obtained PAH concentrations in the gas and particle phases
249 during both seasons are given in Tables (A6 and A7). Total (gas + particle) PAH
250 concentrations varied from 330 - 1770 ng/m³ in the summer season and from 170 - 1290
251 ng/m³ in the winter season with average concentrations of 740 ± 365 and 530 ± 260
252 ng/m³ respectively. Average PAH concentrations were higher than that measured in
253 Chicago, USA (\sum_{26} PAHs = 167 ± 164 ng/m³, Simcik et al. 1999), Harbin, China (\sum_{16}
254 PAHs = 100 ± 94.0 ng/m³, Ma et al. 2010), Guangzhou, China (\sum_{16} PAHs = 340 ± 140
255 ng/m³, Li et al. 2006), Seoul, Korea (\sum_{16} PAHs = 89.3 ± 74.3 ng/m³, Park et al. 2002),
256 Athens, Greece (\sum_{14} PAHs = 28.4 ± 1.63 ng/m³, Vasilakos et al. 2007), Bursa, Turkey
257 during the non-heating season (\sum_{14} PAHs = 150 ng/m³, Esen et al. 2008) and Flanders,
258 Belgium (\sum_{16} PAHs: 57.8 ± 43.0 ng/m³, Ravindra et al. 2006), but lower than those
259 measured at Bursa, Turkey during the heating seasons (\sum_{14} PAHs = 1200 ng/m³. Esen et
260 al. 2008) and in Giza, Egypt (\sum_{14} PAHs = 4300 ng/m³, Hassan and Khoder, 2011). All
261 the above given PAH concentrations represent the sum of the gas phase and particulate
262 phase.

263

264 Gas phase PAH concentrations ranged from 300 - 1400 ng/m³ in the summer season and
265 from 155 - 870 ng/m³ in the winter season with average concentrations of 620 ± 295
266 ng/m³ and 380 ± 170 ng/m³ respectively. Average concentrations at the industrial (845
267 ng/m³) and the traffic sites (640 ng/m³) were slightly higher than at the residential sites
268 (460 ng/m³) during the summer season (Figure 2a). In the winter season, PAH

269 concentrations at the industrial sites (average = 680 ng/m^3) were significantly higher than
270 concentrations at the residential (average = 270 ng/m^3) and the traffic sites (average =
271 365 ng/m^3) (1-way ANOVA, $F = 7.602$, at $\alpha = 0.05$, $p = 0.006$). In both seasons, all the
272 gas phase samples were dominated by 2-3 rings PAHs (parent and alkylated) comprising
273 > 90 % of the total detected concentrations (Khairy and Lohmann, 2012). 4-rings PAHs
274 had a minor contribution (< 11 %) in all the investigated samples. The most abundant
275 PAHs were C₁-Phn/Ant (6.50-34.0 %), Phn (3.70-28.0 %), and C₂-Phn/Ant (4.30-19.4 %)
276 (Figure A1).

277 **Figure 2**

278 Concentrations of PAHs in the particle phase ranged from $27.0 - 340 \text{ ng/m}^3$ in the
279 summer season and from $14.0 - 420 \text{ ng/m}^3$ in the winter season with average
280 concentrations of 120 ± 79.0 and $147 \pm 100 \text{ ng/m}^3$ respectively. In the summer and winter
281 samples, PAH concentrations were significantly higher at the industrial sites (Figure 2b)
282 compared to the traffic and the residential sites (1-way ANOVA, $F_{\text{summer}} = 10.6$, $p =$
283 0.002 ; $F_{\text{winter}} = 26.3$, $p < 0.001$). In contrast to the gas phase PAHs, higher molecular
284 weight PAHs (4, 5 and 6 rings PAHs) and alkylated phenanthrenes predominated in the
285 particle phase (Figure A2).

286

287 **3.2. Temporal variations in PAH concentrations and Meteorological conditions**

288 Figure (2) shows the variations of the gas phase (a) and particulate (b) PAH
289 concentrations during the summer and winter seasons. Concentrations of the gas phase
290 PAHs were significantly higher in the summer (average temperature: 28°C) compared to
291 the winter season (average temperature: 18°C) ($p = 0.003$). This is different from the

292 northern Chinese cities (Ma et al. 2010) with higher PAH concentrations during the
293 heating season (winter) as a result of increased combustion of fossil fuels. In Alexandria,
294 centralized heating systems do not exist and heating of indoor places depends mainly on
295 electric heaters. In contrast to the gas phase PAHs, no statistical significant difference
296 was observed between the summer and winter concentrations of the particle phase PAHs
297 ($p = 0.352$). To investigate the influence of meteorological conditions on the temporal
298 variations in PAH concentrations, recorded temperatures and wind speed at the sampling
299 sites (Table A1) were correlated against gas and particle phase PAH concentrations. As
300 shown in Table (1), gas phase PAH concentrations increased with temperature. In the
301 summer season, there was a marked increase in the enrichment of the gas phase samples
302 with Phn (17 %) and C₁- Phn/Ant (17 %) which could be related to the increase in the
303 evaporative emissions from petroleum products such as asphalt and coal tar sealant
304 (Massei et al., 2005) as a result of the higher temperatures. Gas phase PAHs were also
305 found to decrease with increasing wind speed ($r = -0.46$, $P < 0.01$, $n = 34$). Higher wind
306 speed in the winter season could increase the pollutant dispersion in the atmosphere.
307 Particulate PAH concentrations showed a weak negative correlation with temperature ($r =$
308 -0.15 , $P < 0.01$, $n = 34$). A similar finding was observed in Guiyang, Southwest China
309 (Hu et al. 2012) ($r = -0.17$, $P < 0.05$, $n = 180$). In Alexandria, particulate PAH
310 concentrations were relatively higher in the winter season (Figure 2b) but this difference
311 was statistically insignificant. Based on the strength of the calculated correlation
312 coefficients (moderate to low) in Table (1), we conclude that the temporal variations in
313 the gas phase and particulate PAH concentrations are partially influenced by
314 meteorological conditions, and that the observed temporal variation is mainly attributed

315 to the emission sources. In Alexandria, it is expected that vehicular emissions are the
316 major source of atmospheric PAHs (Barakat, 2002; EEAA, 2011). Although unleaded
317 petrol has recently been used, leaded gasoline is still in use, especially in old vehicles. At
318 the same time, catalytic converters have not yet been extensively introduced to Egypt
319 (EEAA, 2011). The higher PAH concentrations observed during the summer season
320 could be attributed to the marked increase in the traffic density (mainly with gasoline
321 powered vehicles) as a result of the increased number of visitors for recreational purposes
322 (Khairy and Lohmann, 2012). This causes serious congestions on the busy narrow streets
323 as a result of Alexandria's inadequate road networking (Barakat, 2002). Ravindra et al.
324 (2008) indicated that urban areas with congested traffic conditions with vehicles often
325 only traveling short journeys promote the emission of PAHs.

326

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

333

Table 1

3.2 Source apportionment of PAHs

3.2.1. Factor analysis and multiple linear regression

336 The rotated factors of atmospheric PAHs in Alexandria during the summer and winter
337 seasons are presented in Tables (A8 and A9) respectively. In the summer season, four

338 factors were extracted explaining 84.3 % of the total variability in the PAH data. The first
339 factor (Factor 1) accounted for 41.1 % of the total variance and was highly loaded on
340 alkylated phenanthrenes and dibenzothiophenes, BeP, BaP, BbF, BkF, InP Flra and Pyr,
341 which were previously used as tracers for diesel emissions (Li and Khamens, 1993;
342 Larsen and Baker, 2003; Li et al. 2003; Sofowote et al. 2008; Chen et al. 2013). C₁-
343 Phn/Ant was used as the tracer for this factor (for the multiple regression analysis).

344

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

350

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

360

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

370 **3.2.3. Positive matrix factorization (PMF)**

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

384

Figure 3

385 In the summer season, factor 1 accounted for 16.0 % of the sum of the measured PAHs
386 and had good similarities to natural gas emissions. In natural gas combustion, Chry, BaA,
387 Flra, Pyr are expected to be present with low contribution of the high molecular weight
388 PAHs (Simcik et al. 1999; Lee et al. 2004; Ma et al. 2010), as seen in this factor (Figure
389 3a).

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

397

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

407 as a tracer of gasoline emissions (Simcik et al. 1999; Li et al. 2003; Wang et al. 2009;
408 Chen et al. 2013), and less contribution from the 5-rings PAHs compared to the profile of
409 factor 3. Accordingly, Factors 3 and 4 were selected to represent diesel and gasoline
410 emissions respectively.

411

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

419

420 **3.2.4. Unmix model**

421 Four factors during the summer season and three factors during the winter season were
422 extracted by the UNMIX model representing the source profiles, and showed similar
423 results to the PMF model (Figure 3). Factor 1 represented natural gas combustion source
424 (Figure 3e), Factor 2 might be identified as the evaporative/uncombusted petroleum,
425 which appeared in the summer season only (Figure 3f), Factor 3 represented diesel
426 emission source (Figure 3g), and Factor 4 represented gasoline emission source (Figure
427 3h). The estimated average contribution for the extracted sources in the summer and
428 winter seasons was also similar to PMF model (Figure A3).

429

430 **3.2.5. Comparison between the mean source contributions and the predictive ability**
431 **of the FA/MLR, PMF and UNMIX models**

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

442 As shown in Figure (A4), good correlations were found between the predicted PAH
443 concentrations obtained by the three models and the measured PAHs concentration, with
444 $R^2 \geq 0.95$ for both the summer and winter seasons, indicating their strong effectiveness.

445 **3.2.6. Distribution of PAH source contributions**

446 As shown in the estimated average contribution of the extracted sources from the three
447 models (Figure A3), vehicle emissions (diesel + gasoline) were the major source of PAHs
448 to the atmospheric environment of Alexandria with an average contribution of 69.0 % -
449 71.0 % in the winter and summer seasons respectively. In both seasons, diesel emissions
450 were the dominant source, as was indicated in previous studies (Barakat, 2002; Khairy
451 and Lohmann, 2012). Estimated average contributions (ng/m^3) for each source category
452 at the sampling sites using the output of the PMF model are shown in Figure (4). In both

453 seasons, diesel emissions made the largest contribution for PAHs at the industrial sites
454 (Figure 4a), which accounted for an average of 65.0 % of the total measured PAHs
455 concentrations. This is consistent with the higher density of the medium and heavy duty
456 trucks powered by diesel engines that can be observed at the industrial sites. Estimated
457 PAH concentrations that originated from diesel emissions were lower at the traffic and
458 residential sites. However, at 4 of the traffic sites (T2, T3, T8 and T9), and two
459 residential sites (R1, R2), relatively higher diesel emission contributions were observed
460 compared to the other sites. These sites are characterized by higher densities of public
461 transportation buses and medium duty trucks (T2, T3) that are powered by diesel engines
462 compared to the other sites. Diesel emissions accounted for 43.0% and 35.0 % of the total
463 measured PAH concentrations at the traffic and residential sites respectively. Estimated
464 PAH concentrations from the gasoline emission source were higher at the traffic sites
465 (Figure 4b), followed by the residential and industrial sites and accounted for 49.0 %,
466 38.0 % and 22.0 % respectively of the total measured PAH concentrations. Relatively
467 high % contributions from the diesel and gasoline emissions were observed at the
468 residential sites during the summer season. One explanation for that is the that most of
469 the residential sites examined in the current work were either close to a main road with
470 high traffic activity, and/or located in a narrow road with serious congestions (observed
471 during the sampling campaign) enhancing the emission of PAHs (Ravinda et al. 2008).

472

473 Estimated PAH concentrations from the natural gas combustion source, which showed
474 less contribution compared to the other two sources, were higher at the residential sites,
475 followed by the industrial sites (detected at only one site, In2) and the traffic sites, and

476 accounted for 27.0 %, 13.0 % and 9.00 % respectively of the total PAH concentrations.
477 These findings seem reasonable as the natural gas is used as the energy source in home
478 appliances and in industrial plants (EEAA, 2011).

479 **Figure 4**

480 No seasonal trends were observed for the estimated PAH concentrations from the diesel
481 emissions and the natural gas combustion emission sources at all the sites in Alexandria
482 (Figure 4a,c). However, estimated PAH concentrations from the gasoline emissions were
483 significantly higher in the summer season at the traffic ($P = 0.027$) and residential sites (P
484 $= 0.015$) (Figure 4b), which is attributed to the higher traffic density during the summer
485 season as a result of the increased number of visitors for recreational purposes (Khairy
486 and Lohmann, 2012). Overall, obtained source distributions were closely related to the
487 human activities around the sampling sites (Khairy and Lohmann 2012).

488

489 **3.3. Cancer risk assessment from the exposure to atmospheric PAHs**

490

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

496 Estimates of the lifetime average daily dose (LADD) and the incremental lifetime cancer
497 risks (ILTCR) for the inhalation, ingestion and dermal exposure routes are given in
498 Tables (A12, A13 and A14) respectively. Greater possibility of occurrence of adverse

499 health effects were associated with the dermal ($ILTCR_{der}$) contact to atmospheric PAHs
500 (6.48×10^{-3} - 4.41×10^{-2}), followed by the ingestion exposure route ($ILTCR_{ing}$) ($1.31 \times$
501 10^{-5} - 8.92×10^{-5}), and finally the inhalation exposure route ($ILTCR_{inh}$) (1.08×10^{-6} - 5.88
502 $\times 10^{-6}$). Calculated total incremental lifetime cancer risks (TILTCR) are shown in Figure
503 (5). All the calculated values at all the sites were higher than 10^{-3} , which greatly exceed
504 the USEPA acceptable level of 10^{-6} (USEPA, 2004) indicating high potential
505 carcinogenic health risk. It was obvious that the dermal contact exposure route was the
506 major contributor to the total lifetime cancer risk comprising > 99 % of the calculated
507 values of TILTCR at all the investigated sites. Concerning the individual toxicity of the
508 target PAHs, the compounds that contributed most to the total estimated risk were BbF
509 (81.3–94.0 %) and BaP (5.00-12.5 %), which were associated with vehicular emissions
510 (Figure 3). We therefore conclude that the cancer risk associated with the exposure to
511 PAHs emitted from vehicle emissions is not negligible and should be taken into account
512 for health protection in the future.

513 Figure 5

514 **4. Conclusions**

515 Urban cities are large sources of atmospheric pollution. Understanding the seasonal
516 variability in the sources of atmospheric PAHs requires the existence of emission
517 inventories, which in terms will help to develop efficient pollution control strategies and
518 assist in the protection of the human health. Our results indicted that the atmospheric
519 environment of Alexandria, Egypt is highly polluted with PAHs, with concentrations
520 much higher that in other urban cities worldwide. The spatial distribution of PAHs,
521 temporal variations and source apportionment results indicated that vehicle emissions,

522 especially from diesel powered engines are the major source of PAHs in Alexandria.
523 Although the three receptor models gave comparable results with good matching between
524 the predicted and measured PAH concentrations, PMF and UNMIX models are more
525 reliable and accurate than the FA/MLR model which is associated with a higher degree of
526 uncertainty because of the independence of the calculations on the quality assurance data
527 and the negative loadings constrains. Based on our findings, at least two receptor models
528 should be used to confirm the output of the source apportionment. Our results also
529 indicated that there is a high potential risk of cancer development as a result of the
530 exposure to PAHs via inhalation, ingestion and dermal contact and that PAH exposures is
531 not negligible and should be taken into account for health protection in the future.

532

533 **Appendix. Supplementary data**

534

535 **5. References**

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