Receptor modelling study of polycyclic aromatic hydrocarbons in Jeddah, Saudi Arabia

Alghamdi, Mansour A.; Alam, Mohammed S.; Yin, Jianxin; Stark, Christopher; Jang, Eun-Hwa; Harrison, Roy M.; Shamy, Magdy; Khoder, Mamdouh I.; Shabbaj, Ibrahim I.

DOI:
[10.1016/j.scitotenv.2014.10.056](https://doi.org/10.1016/j.scitotenv.2014.10.056)

License:
None: All rights reserved

Document Version
Peer reviewed version

Citation for published version (Harvard):
Alghamdi, MA, Alam, MS, Yin, J, Stark, C, Jang, E-H, Harrison, RM, Shamy, M, Khoder, MI & Shabbaj, II 2015, 'Receptor modelling study of polycyclic aromatic hydrocarbons in Jeddah, Saudi Arabia', *Science of the Total Environment*, vol. 506-507, pp. 401-408. <https://doi.org/10.1016/j.scitotenv.2014.10.056>

[Link to publication on Research at Birmingham portal](#)

Publisher Rights Statement:

NOTICE: this is the author's version of a work that was accepted for publication in Science of The Total Environment. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Science of The Total Environment, Vol 506-7, February 2015, pp. 401-8.
DOI: 10.1016/j.scitotenv.2014.10.056

Eligibility for repository checked January 2015

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

Receptor Modelling Study of Polycyclic Aromatic Hydrocarbons in Jeddah, Saudi Arabia

Mansour A. Alghamdi¹, Mohammed S. Alam^{2*}, Jianxin Yin²,
Christopher Stark², Eunhwa Jang², Roy M. Harrison^{1,2*†},
Magdy Shamy¹, Mamdouh I. Khoder^{1,†}, Ibrahim I. Shabbaj¹

¹ Department of Environmental Sciences, Faculty of Meteorology,
Environment and Arid Land Agriculture, King Abdulaziz University,
Jeddah, Saudi Arabia

² Division of Environmental Health & Risk Management
School of Geography, Earth & Environmental Sciences
University of Birmingham
Edgbaston, Birmingham, B15 2TT
United Kingdom

* To whom correspondence should be addressed (Tel: +44 121 414 3494; Fax: +44 121 414 3709;
Email: r.m.harrison@bham.ac.uk) or m.s.alam@bham.ac.uk

† Also at: Center of Excellence in Environmental Studies, King Abdulaziz University, Jeddah, 21589, Saudi Arabia

21 **ABSTRACT**

22 Measurements of 14 polycyclic aromatic hydrocarbons (PAH) have been made in Jeddah, Saudi
23 Arabia, with a view to establishing the concentrations in this major city, and quantifying the
24 contributions of major sources. Particulate and vapour forms have been sampled and analysed
25 separately. The concentrations are compared to measurements from other sites in the Middle Eastern
26 region and are towards the lower end of the range, being far lower than concentrations reported from
27 Riyadh (Saudi Arabia), Assiut (Egypt) and Tehran (Iran) but broadly similar to those measured in
28 Damascus (Syria) and higher than those measured in Kuwait. The partitioning between vapour and
29 particle phases is similar to that in data from Egypt and China, but with many compounds showing a
30 higher particle-associated percentage than in Birmingham (UK) possibly reflecting a higher
31 concentration of airborne particulate matter in the former countries. Concentrations in Jeddah were
32 significantly higher at a site close to the oil refinery and a site close to a major ring road than at a
33 suburban site to the north of the city. Application of Positive Matrix Factorisation to the pooled data
34 elicited three factors accounting respectively for 17%, 33% and 50% of the measured sum of PAH and
35 these are interpreted as arising from gasoline vehicles, industrial sources, particularly the oil refinery,
36 and to diesel/fuel oil combustion.

37

38 **Keywords:** Polycyclic aromatic hydrocarbons; PAH; Positive Matrix Factorisation; PMF; Source
39 apportionment

40

41

42

43 1. INTRODUCTION

44 Polycyclic aromatic hydrocarbons (PAH) have generated a great deal of interest over several decades
45 owing to their known carcinogenic and mutagenic properties (Giger and Blumer, 1974). PAH are
46 ubiquitous pollutants, present in the atmosphere in the vapour phase and associated with particulate
47 matter (Harrison et al., 1996), as well as in other environmental media and foodstuffs. PAH congeners
48 are mainly formed through incomplete combustion or pyrolysis of organic material and many have
49 mutagenic and carcinogenic properties, leading to many human health concerns (Collins et al., 1998).
50 Major anthropogenic sources include both stationary sources such as industrial and domestic
51 combustion, and mobile sources including road traffic. PAH have multiple point and diffuse sources,
52 and unlike other persistent organic pollutants, cannot be controlled by the introduction of substitute
53 chemicals (Jang et al., 2013). With the percentage of the population living in urban areas increasing
54 and liable to exposure to elevated concentrations of PAH, it is important to understand and assess the
55 occurrence and sources of PAH.

56
57 Numerous studies have assessed different methods of source apportionment, in an attempt to devise
58 efficient strategies to reduce pollution of the urban atmosphere by PAH. For example, diagnostic ratios
59 have been utilised to identify pyrogenic or petrogenic sources (Zhang et al., 2005), diesel or gasoline
60 sources (El-Mubarak et al., 2014), fuel or combustion (De La Torre-Rouche et al., 2009) and traffic
61 related sources (Katsoyiannis et al., 2007) and this work has recently been reviewed by Tobiszewski
62 and Namiesnik (2012). Further studies, however, have highlighted the variable range of emission
63 factors and compound ratios from given source categories, deeming this method of source
64 apportionment imprecise (Katsoyiannis et al., 2011). In addition, more recent studies have suggested
65 that diagnostic ratios are a useful tool for assessing atmospheric reactivity of PAH, rather than source
66 apportionment, as these ratios are subject to small changes as the distance from the original source

increases (Alam et al., 2013; Alam et al., 2014; Keyte et al., 2013; Katsoyiannis and Breivik, 2014). Principal component analysis (PCA) has also been utilised as a source apportionment method which separates chemical constituents of the atmosphere according to their source using a statistical factor analysis method (Hopke et al., 2006; Mari et al., 2010). However, PCA is subject to drawbacks including the issue of negative solutions. This has been subsequently overcome by using positive matrix factorisation (PMF) as the preferred technique of source apportionment of atmospheric constituents (Jang et al., 2013; Dvorska et al., 2012). The other commonly used source apportionment method, the Chemical Mass Balance model, requires locally generated PAH source profiles which were not available.

A vast number of measurements of airborne concentrations of PAH have been reported from various geographical locations, including UK, Europe, USA and China. However, very little information has been reported from the Middle East. The environmental concerns of Saudi Arabia, in particular, are increasing with increasing developmental activity (Magram et al., 2009). Jeddah, the second largest city and most significant commercial centre in Saudi Arabia, has experienced a rapid and diverse growth over the last thirty years and has been accompanied by environmental degradation. Air quality has progressively deteriorated and the number of vehicles has increased to more than 1.4 million (Saudi Network, 2008). The city's major stationary PAH sources include a desalination plant, a power generation plant and an oil refinery. The oil refinery was originally built in a non residential area, but with urbanisation, is now in the middle of a highly populated area (Al-Jahdal and Bisher, 2008).

In this study, we report the airborne concentration of 14 PAH compounds in both vapour and particulate phases in Jeddah, Saudi Arabia. Three sampling locations were chosen according to their proximity to the Jeddah oil refinery and data were collected simultaneously. Positive matrix factorisation is utilised to separate the chemical constituents according to their congener profile and the results are discussed in terms of likely source categories.

2. EXPERIMENTAL

2.1 Site Location

Sampling was conducted simultaneously at three locations in Jeddah, the second largest city and most significant commercial centre in the Kingdom of Saudi Arabia, with a population of *ca.* 3.4 million.

The sampling sites are shown in Figure 1. ~~The locations were chosen according to their distance from the Jeddah oil refinery.~~ *Site A* was a primary school situated in a highly populated economically disadvantaged residential area, located in the Ghulail district, south of the city and *ca.* 700 m east of the Jeddah oil refinery. *Site B* was a primary school, located in the Al-Muntazahat district, East of Jeddah, *ca.* 150 m adjacent to the heavily trafficked Al-Haramain ring road. *Site C* was an urban background site located in the Al-Murjan district, situated on the Red Sea Creek (Sharm Obhur), and is subjected to anthropogenic emissions from some moderately busy roads (nearest road *ca.* 300 m away) and surrounding activities from a few local residents. The samplers at all sites were located at a height of *ca.* 9 m above street level. This was to ensure that contaminated road dust was not sampled, and to ensure that samplers were not interfered with.

2.2 Sample Collection

Daily (24 h) samples were collected simultaneously at the three sampling locations between 23 February 2013 and 23 April 2013, using a polyurethane foam high volume air sampler (TE-PUF, Tisch Environmental, Inc). The sampler typically draws volumes of air in the range of 240 – 300 m³ over a 24 h period, through a quartz microfibre filter (TE-QMA4 10.16 cm) substrate, to collect compounds in the particulate phase, followed by an absorbent polyurethane foam (PUF) substrate, to collect compounds present in the gaseous phase. Temperatures during the study ranged between 26 and 30 °C for all three sites.

115 2.3 Sample Analyses

116 Prior to sampling, the filters were preheated at 400 °C for 48 h in a box furnace, wrapped in clean
117 preheated foil, placed in a cardboard box and sealed in an airtight metallic container. The PUF
118 substrates were pre-cleaned prior to their use in the field by immersing in 100 mL of dichloromethane
119 (DCM) and ultrasonicated at 20 °C for 30 min. The solvent was then drained and the PUF substrates
120 were left to dry in a sealed metal container under a stream of nitrogen. The clean and dry PUF
121 substrates were subsequently sealed in airtight plastic bags and stored in the freezer. Once exposed, the
122 filter and PUF substrates were wrapped separately with clean preheated foil, enclosed in airtight plastic
123 bags and stored at approximately -18 °C.

124
125 Samples were analysed for 14 PAH using the methodology described previously (Delgado-Saborit et
126 al., 2013). Briefly, filter and PUF substrates were spiked with 1000 pg μL^{-1} deuterated internal
127 standards for quantification (see Supplementary Material for a list of these compounds). Filters were
128 immersed in DCM and ultrasonicated for 15 min at 20 °C. The extract was subsequently dried and
129 cleaned using a chromatography column filled with 0.5 g of anhydrous sodium sulphate (puriss grade
130 for HPLC). The extract was further concentrated to 50 μL under a gentle N_2 flow. PUF substrates were
131 immersed in 100 mL of DCM and ultrasonicated for 20 min at 20 °C. The sample was then
132 concentrated to 10 mL using N_2 and subsequently dried and cleaned as outlined for the filters above.

133 Samples were analysed for PAH compounds using Gas Chromatography (6890, Agilent Technologies)
134 equipped with a non-polar capillary column (Agilent HP-5MS, 30m, 0.25 mm ID, 0.25 μm film
135 thickness – 5 % phenylpolysiloxane) in tandem with a Mass Spectrometer (5973N, Agilent
136 Technologies). The precision of analysis was 8±4% and the accuracy, expressed as the difference
137 between the measured and true value as a percentage of the true value was 6±4%. The analytical
138 detection limits varied widely between congeners, and sample detection limits estimated from analysis

of blank filters and PUFs all lay well below 1 pg m⁻³ for the 24-hour air samples. Further information regarding the analytical procedure can be found in Delgado-Saborit et al., 2013.

2.4 Positive Matrix Factorisation (PMF)

PMF is a multivariate receptor model that is used 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, and is defined as follows:

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij}$$

where x_{ij} is the j_{th} measured species concentration in the i_{th} sample, g_{ik} is the factor contribution of k source to i_{th} sample, f_{kj} is the fraction of j species in the k source, and e_{ij} is the residuals matrix. PMF is described in detail elsewhere (Paatero and Tapper, 1994; Paatero, 1997). Briefly, it is weighted least square fit, to search for a proper residual matrix by minimising the object function, $Q(E)$, as follows (Hopke, 2001):

$$Q(E) = \sum_{i=1}^m \sum_{j=1}^n \left(\frac{E_{ij}}{\partial_{ij}} \right)^2$$

where ∂_{ij} is the estimated uncertainty associated with the determination of x_{ij} and E_{ij} is the scaled residual defined as:

$$E_{ij} = x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}$$

Appropriate uncertainties, ∂_{ij} , are imperative for PMF analyses, where the user has the freedom to generate the ∂ matrix based on method detection limits and uncertainties in the measurements. Information regarding method detection limits and uncertainties in the chemical measurements, which

were applied to these data, are described elsewhere (Delgado-Saborit et al., 2013). The robust mode is the default mode with EPA PMF v3.0, which reduces the effect of very large variables by treating them as outliers so that they do not affect the model fitting process and results (Sofowote et al., 2011).

Multiple f and g matrices with the same minimum Q value can exist, and thus the least squares approach can produce multiple solutions depending on the initial starting point (Jang et al., 2013; Sofowote et al., 2011). In order to estimate a statistically stable solution, factor rotation by changing F_{peak} values from -1.4 and 0.3 was conducted, as well as utilising the bootstrapping technique, within EPA PMF v3.0 software, based on arbitrary selection of n samples from the data. More details on bootstrapping factor profiles, rotations and other features of PMF can be found elsewhere (Norris et al., 2008).

166

3. RESULTS AND DISCUSSION

3.1 PAH Concentrations

The average total (vapour and particulate) concentration of PAH measured at the three sampling sites between 23 February and 23 April ~~2012~~ 2013 are shown in Table 1. Concentrations measured at sites A and B were statistically larger (t test, $p < 0.01$) than those measured at site C, where average total concentrations for all PAH measured at site C were between 50 and 90 % lower (see Table 1). Total concentrations measured at site A were significantly larger (t test, $p < 0.05$) to those at site B, with the exception of ANT and B(a)A, where no significant difference was observed. This demonstrates the importance of oil refinery and traffic related emissions of PAH. Lower molecular weight (LMW) PAH compounds ($Da < 202$) were predominantly in the vapour phase, where the most abundant PAH measured at the three sites were PHE, FLU and PYR, in agreement with previous measurements from Western Europe, the Middle East and China (Albinet et al., 2007; Gevaio et al., 2006; Ma et al., 2011).

179 The concentrations of vapour phase LMW PAH were largest at site A followed by B and C, with the
180 exception of ANT, which was frequently (~53 %) larger at site B. Higher molecular weight (HMW)
181 PAH compounds ($Da > 228$) were predominantly in the particulate phase, with B(ghi)P and COR being
182 the most abundant at sites A and B, and B(ghi)P and CHR being the two most abundant PAH at site C.
183 This suggests that sites A and B may be associated with high levels of vehicular emissions, as B(ghi)P
184 and COR are often used as vehicular emission tracers (Greenberg et al., 1981; Harkov et al., 1984).
185 Furthermore, although HMW PAH in the particulate phase (B(b)F to COR) were statistically different
186 between all sites, LMW PAH in the particulate phase (PHE to CHR) were remarkably similar for sites
187 A and B (within 10 %).

188

189 Table 2 summarises the PAH concentrations measured in Jeddah and some other cities around the
190 world. The average total suspended particulate (TSP) concentration for sites A, B and C were 435, 396,
191 $232 \mu\text{g}/\text{m}^3$, reflecting the large crustal dust component present in particulate matter in the Middle
192 Eastern area. The measured PAH concentrations, however, are only modestly higher than those
193 measured in urban areas of the United Kingdom (Delgado-Saborit et al., 2013; Alam et al., 2013), and
194 significantly lower than those previously measured in different areas of Saudi Arabia (El-Mubarak et
195 al., 2014; Habeebullah, 2013). Habeebullah (2013) conducted a risk assessment of PAH in Makkah,
196 located *ca.* 85 km east of Jeddah, during an influx of approximately 2.8 million pilgrims to the city, in
197 November 2010. They reported total particulate PAH concentrations in the range of 103.5 to 195.2
198 ng/m^3 , a factor of 17 to 33 times larger than Site A in this study. These high concentrations were
199 attributed to various residential activity and traffic emissions. Makkah City, however, has been subject
200 to extensive building construction since 2009, particularly in the vicinity of two of their sampling sites,
201 which may also give rise to the elevated levels reported in their study. In a more recent study, El-
202 Mubarak et al. (2014) reported PM_{10} PAH concentrations in Riyadh, located *ca.* 1000 km north east of

203 Jeddah, in December 2010. The authors reported extremely high concentrations of individual PAH
204 congeners of up to 1003 ng/m³, with an average concentration of B(a)P of 400 ng/m³, three orders of
205 magnitude larger than this study (0.39 ng/m³ for site A). Furthermore, Abdallah et al. (2014)
206 investigated gaseous and particulate PAH concentrations across 9 sampling locations in Assiut, Egypt
207 and reported total mean concentrations of B(a)P of up to 108.2 ng/m³ in high population density areas.
208 The large concentrations measured were attributed to vehicular exhaust emissions which was also
209 highlighted by Hasan and Khoder (2012) who reported total mean concentrations for B(a)P and
210 B(ghi)P of 159.55 and 219.32 ng/m³, respectively; at a traffic related site in Giza, Egypt.

211

212 Concentrations reported from Middle Eastern countries other than Egypt and other parts of Saudi
213 Arabia are also relatively higher than those reported in this study. Total mean concentrations of PHE,
214 B(a)P and B(ghi)P in Tehran, Iran were 278.19, 18.71 and 34.38 ng/m³ where the major emission
215 sources are thought to be traffic-related (Halek et al., 2010). In Damascus, Syria, the concentration of
216 particulate B(a)P and B(ghi)P was ~ 4.5 and 5.2 ng/m³, respectively (Dimashki et al., 1996). However,
217 PAH concentrations reported from Kuwait were lower than those in this study (Gevao et al., 2006),
218 where average airborne concentrations were in the range of 2.63 ng/m³ (for PHE) and 0.07 ng/m³ (for
219 D(ah)A). The authors also reported that approximately 70 to 90 % of the total PAH concentration
220 consisted of PHE, FLU and PYR, and a substantial increase in the contribution of HMW PAH to the
221 total PAH was observed at sites closer to the oil lakes of Kuwait.

222

223 The influences upon the partitioning of PAH between the vapour and condensed phases need to be
224 considered as PAH are known to cycle actively between the particle and vapour phases. There have
225 been various theoretical treatments of these processes reviewed in Keyte et al. (2013), the simplest
226 being due to Yamasaki et al. (1982), which can be expressed as:

$$\log[A(TSP)F^{-1}] = -mT^{-1} + c$$

in which A is the gas-phase concentration, TSP is total suspended particulate matter, F is the particulate (filter) concentration, T is the sampling temperature (K), and m and c are compound-dependent empirical constants. From this, it may be seen that an increase in temperature will be associated with a relative increase in vapour (A/F increases), and an increase in TSP leads to a reduction in vapour (A/F decreases).

Figure 2 shows the percentage particulate PAH in various locations. The data from Jeddah are very similar to those from Egypt [\(Giza and Asiut\)](#) and China [\(Wanqingsha\)](#), but for the lower molecular weight compounds have a higher particulate component than in the data from Birmingham (UK). This seems likely to be reflective of the higher TSP loading in Jeddah causing greater partitioning into the particle phase, outweighing the effect of temperature in increasing the vapour phase component, [as TSP concentrations in Birmingham are generally \$< 30 \mu\text{g m}^{-3}\$ \(unpublished data\)](#).

3.2 PMF Modelling

A 52×14 matrix (sample number $\times$ 14 PAH species) dataset was introduced into the EPA PMF v3.0 software to assess the source contribution to PAH. Total PAH (vapour + particulate) was used to minimise the influence of partitioning, ageing and photochemical degradation (Kim et al., 2009). Uncertainties applied to the data corresponded to the calculated limits of detection and recovery standard deviation of the surrogate standards as outlined in Delgado-Saborit et al. (2013) and as modified by Jang et al. (2003) to give less weight to the more reactive compounds, which are expected

249 to degrade appreciably between source and receptor. Three source factors were extracted from the PMF
250 model, illustrated in Figure 3.

251

252 Factor 1 accounted for 17 % of the sum of the measured PAH species and was attributed to traffic
253 emissions, in particular gasoline powered vehicles. The profile (see Figure 3) includes conventional
254 traffic biomarkers including B(a)P, B(ghi)P and COR (Greenberg et al., 1981; Harkov et al., 1984;
255 Mastral et al., 2003; Ning et al., 2007). A strong temporal profile was also observed in this factor with
256 average concentration levels during weekdays being significantly larger for the sum of PAH (Σ PAH)
257 and B(a)P than at weekends (Figure 4).

258

259 Factor 2 was attributed to industrial sources, in particular the oil refinery, and accounted for up to 33 %
260 of the sum of the measured PAH species. This factor was dominated by FLU, PYR and D(ah)A and did
261 not show a significant difference between weekdays and weekends. The UK National Atmospheric
262 Emissions Inventory (<http://naei.defra.gov.uk/>) reports relatively large emissions of FLU from refinery
263 combustion between 2002 and 2006, in agreement with Factor 2 from this study. Kulkarni and
264 Venkataraman, (2000) reported the significance of FLU and PYR emissions from oil combustion
265 activities and the predominance of B(a)P, PYR and D(ah)A from kerosene uses. Furthermore, in a
266 recent PMF study of urban air in the UK, it was reported that only a small concentrations of D(ah)A
267 could be attributed to the net traffic contribution (Jang et al., 2013). This factor was responsible for the
268 largest contribution at site A, which is located *ca.* 700 m from Jeddah's oil refinery. Site specific plots
269 and weekday-weekend variation are shown in Figure 4.

270

271 Factor 3 accounted for 50 % of the sum of the measured PAH species and was dominated by LMW
272 PAH compounds (PHE, ANT, FLU, B(a)A and CHR). A strong temporal profile was also observed in

this factor with average concentration levels during weekdays being significantly larger for Σ PAH and B(a)P than at weekends (Figure 4). This factor was responsible for PAH concentrations in the order, site B > site A > site C. The predominance of PHE along with FLU, CHR and PYR have been previously reported as diesel exhaust markers and thus been associated with diesel traffic emissions (Riddle et al., 2008; Zielinska et al., 2004). However, enhanced levels of LMW PAH species have also been attributed to oil combustion (Lee et al., 2004). In comparison to a previously reported diesel combustion derived source profile from the UK NAEI (Jang et al., 2013), factor 3 has a larger contribution of ANT, B(a)A and CHR, which may be explained by the use of different compositions of diesel fuels between the UK and Saudi Arabia. Alternatively, the enhanced levels of LMW PAH observed in factor 3 may be due to both oil combustion, originating from Jeddah's desalination plant, and diesel traffic emissions, with a possible contribution from shipping, which burns predominantly heavy fuel oils. This would affect predominantly site 1 which is close to the port. The desalination plant is situated central to all three sites (see Figure 1) and the prevailing north westerly winds means that the emissions from the plant may affect mainly the sites A and B.

4. CONCLUSION

The concentrations of PAH measured in Jeddah are overall surprisingly similar to those in Birmingham (UK) and Wanqingsha (China), while being higher than those reported for Kuwait, but far below the measurements reported for Assuit and Giza (Egypt) and Tehran (Iran) (see Table 2). Concentrations decline from site A close to the oil refinery to site B which was close to the ring road, which are both significantly higher than those at site C which was in a suburban area in the north of the city. The partitioning of PAH between the particle and vapour phases is broadly similar to that in many other studies but shows some preferential partitioning into particles especially for low molecular weight compounds compared to the data from Birmingham (UK). This is attributed to the very much higher

297 concentrations of total suspended particulate matter (TSP) in Jeddah in comparsion to Birmingham
298 with the influence of the higher temperatures in Jeddah being a secondary effect tending towards higher
299 vapour concentrations.

300
301 The source apportionment study, which is one of the very few successful published applications of
302 PMF to PAH datasets, clearly shows three major source contributions. The largest appears to be from
303 combustion of diesel and fuel oil, the former probably predominantly in road vehicles while there may
304 be a significant contribution from the Jeddah desalination plant to the latter. The second largest
305 contribution is from refinery emissions while the third contribution, which shows a strong weekday to
306 weekend variation, is attributed to gasoline vehicle emissions.

307

308 **ACKNOWLEDGMENT**

309 This paper was funded by King Abdulaziz University (KAU), Jeddah, under grant no. (3-10-1432/
310 HiCi). The authors, therefore, acknowledge technical and financial support of KAU.

311

REFERENCES

- Abdallah, M.-E., Atia, N., 2014. Atmospheric concentrations, gaseous–particulate distribution, and carcinogenic potential of polycyclic aromatic hydrocarbons in Assiut, Egypt. *Environmental Science and Pollution Research*, 1-11. DOI 10.1007/s11356-014-2746-6.
- Al-Jahdali, M., Bashir, A., 2008. Sulfur dioxide accumulation in soil and plant leaves around an oil refinery: A case study from Saudi Arabia. *American Journal of Environmental Sciences* 4, 84-88.
- Alam, M.S., Delgado-Saborit, J.M., Stark, C., Harrison, R.M., 2013. Using atmospheric measurements of PAH and quinone compounds at roadside and urban background sites to assess sources and reactivity. *Atmospheric Environment* 77, 24-35.
- Alam, M.S., Delgado-Saborit, J.M., Stark, C.P., Harrison, R.M., 2014. Investigating PAH relative reactivity using congener profiles, quinone measurements and back trajectories. *Atmos. Chem. Phys.* 14, 2467-2477.
- Albinet, A., Leoz-Garziandia, E., Budzinski, H., Villenave, E., 2007. Polycyclic aromatic hydrocarbons (PAHs), nitrated PAHs and oxygenated PAHs in ambient air of the Marseilles area (South of France): Concentrations and sources. *Science of the Total Environment* 384, 280-292.
- Callen, M.S., de la Cruz, M.T., Lopez, J.M., Murillo, R., Navarro, M.V., Mastral, A.M., 2008. Some inferences on the mechanism of atmospheric gas/particle partitioning of polycyclic aromatic hydrocarbons (PAH) at Zaragoza (Spain). *Chemosphere* 73, 1357-1365.
- Collins, J.F., Brown, J.P., Alexeeff, G.V., Salmon, A.G., 1998. Potency equivalency factors for some polycyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbon derivatives. *Regulatory Toxicology and Pharmacology* 28, 45-54.
- De La Torre-Roche, R.J., Lee, W.-Y., Campos-Diaz, S.I., 2009. Soil-borne polycyclic aromatic hydrocarbons in El Paso, Texas: Analysis of a potential problem in the United States/Mexico border region. *Journal of Hazardous Materials* 163, 946-958.
- Delgado-Saborit, J.M., Alam, M.S., Pollitt, K.J.G., Stark, C., Harrison, R.M., 2013. Analysis of atmospheric concentrations of quinones and polycyclic aromatic hydrocarbons in vapour and particulate phases. *Atmospheric Environment* 77, 974-982.
- Dimashki, M., Smith, D.J.T., Harrison, R.M., 1996. Urban levels of polycyclic aromatic hydrocarbons and nitro-PAH in atmospheric particles sampled from Birmingham, UK and Damascus, Syria. *Polycyclic Aromatic Compounds* 9, 201-208.
- Dvorska, A., Komprdova, K., Lammel, G., Klanova, J., Placha, H., 2012. Polycyclic aromatic hydrocarbons in background air in central Europe - Seasonal levels and limitations for source apportionment. *Atmospheric Environment* 46, 147-154.

- El-Mubarak, A.H., Rushdi, A.I., Al-Mutlaq, K.F., Bazeyad, A.Y., Simonich, S.L.M., Simoneit, B.R.T., 2014. Identification and source apportionment of polycyclic aromatic hydrocarbons in ambient air particulate matter of Riyadh, Saudi Arabia. *Environmental Science and Pollution Research* 21, 558-567.
- Gevao, B., Al-Omair, A., Sweetman, A., Al-Ali, L., Al-Bahloul, M., Helaleh, M., Zafar, J., 2006. Passive sampler-derived air concentrations for polybrominated diphenyl ethers and polycyclic aromatic hydrocarbons in Kuwait. *Environmental Toxicology and Chemistry* 25, 1496-1502.
- Giger, W., Blumer, M., 1974. Polycyclic aromatic hydrocarbons in environment - isolation and characterization by chromatography, visible, ultraviolet, and mass-spectrometry. *Analytical Chemistry* 46, 1663-1671.
- Greenberg, A., Bozzelli, J.W., Cannova, F., Forstner, E., Giorgio, P., Stout, D., Yokoyama, R., 1981. Correlations between lead and coronene concentrations at urban, suburban, and industrial sites in New-Jersey. *Environmental Science & Technology* 15, 566-570.
- Habeebullah, T.M., 2013. Risk assessment of poly cyclic aromatic hydrocarbons in the Holy City of Makkah, Saudi Arabia. *International Journal of Environmental Science and Development* 4, 139-142.
- Halek, F., Kianpour-rad, M., Kavousi, A., 2010. Characterization and source apportionment of polycyclic aromatic hydrocarbons in the ambient air (Tehran, Iran). *Environmental Chemistry Letters* 8, 39-44.
- Harkov, R., Greenberg, A., Darack, F., Daisey, J.M., Lioy, P.J., 1984. Summertime variations in polycyclic aromatic-hydrocarbons at 4 sites in New-Jersey. *Environmental Science & Technology* 18, 287-291.
- Harrison, R.M., Smith, D.J.T., Luhana, L., 1996. Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK. *Environmental Science & Technology* 30, 825-832.
- Hassan, S.K., Khoder, M.I., 2012. Gas-particle concentration, distribution, and health risk assessment of polycyclic aromatic hydrocarbons at a traffic area of Giza, Egypt. *Environmental Monitoring and Assessment* 184, 3593-3612.
- Hopke, P.K., 2001. A guide to positive matrix factorization <http://www.epa.gov/ttnamti1/files/ambient/pm25/workshop/laymen.pdf>.
- Hopke, P.K., Ito, K., Mar, T., Christensen, W.F., Eatough, D.J., Henry, R.C., Kim, E., Laden, F., Lall, R., Larson, T.V., Liu, H., Neas, L., Pinto, J., Stolzel, M., Suh, H., Paatero, P., Thurston, G.D., 2006. PM source apportionment and health effects: 1. Intercomparison of source apportionment results. *Journal of Exposure Science and Environmental Epidemiology* 16, 275-286.
- Huang, B., Liu, M., Bi, X., Chaemfa, C., Ren, Z., Wang, X., Sheng, G., Fu, J., 2014. Phase distribution, sources and risk assessment of PAHs, NPAHs and OPAHs in a rural site of Pearl River Delta region, China. *Atmospheric Pollution Research* 5, 210-218.

- Jang, E., Alam, M.S., Harrison, R.M., 2013. Source apportionment of polycyclic aromatic hydrocarbons in urban air using positive matrix factorization and spatial distribution analysis. *Atmospheric Environment* 79, 271-285.
- Katsoyiannis, A., Breivik, K., 2014. Model-based evaluation of the use of polycyclic aromatic hydrocarbons molecular diagnostic ratios as a source identification tool. *Environmental Pollution* 184, 488-494.
- Katsoyiannis, A., Sweetman, A.J., Jones, K.C., 2011. PAH Molecular Diagnostic Ratios Applied to Atmospheric Sources: A Critical Evaluation Using Two Decades of Source Inventory and Air Concentration Data from the UK. *Environmental Science & Technology* 45, 8897-8906.
- Katsoyiannis, A., Terzi, E., Cai, Q.-Y., 2007. On the use of PAH molecular diagnostic ratios in sewage sludge for the understanding of the PAH sources. Is this use appropriate.? *Chemosphere* 69, 1337-1339.
- Keyte, I.J., Harrison, R.M., Lammel, G., 2013. Chemical reactivity and long-range transport potential of polycyclic aromatic hydrocarbons - a review. *Chemical Society Reviews* 42, 9333-9391.
- Kim, D., Kumfer, B.M., Anastasio, C., Kennedy, I.M., Young, T.M., 2009. Environmental aging of polycyclic aromatic hydrocarbons on soot and its effect on source identification. *Chemosphere* 76, 1075-1081.
- Kulkarni, P., Venkataraman, C., 2000. Atmospheric polycyclic aromatic hydrocarbons in Mumbai, India. *Atmospheric Environment* 34, 2785-2790.
- Lee, J.H., Gigliotti, C.L., Offenberg, J.H., Eisenreich, S.J., Turpin, B.J., 2004. Sources of polycyclic aromatic hydrocarbons to the Hudson River Airshed. *Atmospheric Environment* 38, 5971-5981.
- Ma, W.-L., Sun, D.-Z., Shen, W.-G., Yang, M., Qi, H., Liu, L.-Y., Shen, J.-M., Li, Y.-F., 2011. Atmospheric concentrations, sources and gas-particle partitioning of PAHs in Beijing after the 29th Olympic Games. *Environmental Pollution* 159, 1794-1801.
- Magram, S.F., 2009. A review on the environmental issues in Jeddah, Saudi Arabia with special focus on water pollution. *Journal of Environmental Science and Technology* 2, 120-132.
- Mari, M., Harrison, R.M., Schuhmacher, M., Domingo, J.L., Pongpiachan, S., 2010. Inferences over the sources and processes affecting polycyclic aromatic hydrocarbons in the atmosphere derived from measured data. *Science of the Total Environment* 408, 2387-2393.
- Mastral, A.M., Lopez, J.M., Callen, M.S., Garcia, T., Murillo, R., Navarro, M.V., 2003. Spatial and temporal PAH concentrations in Zaragoza, Spain. *Science of the Total Environment* 307, 111-124.
- Ning, Z., Geller, M.D., Moore, K.F., Sheesley, R., Schauer, J.J., Sioutas, C., 2007. Daily variation in chemical characteristics of urban ultrafine aerosols and inference of their sources. *Environmental Science & Technology* 41, 6000-6006.

- Norris, G., Vendantam, R., Wade, K., Brown, S., Prouty, J., Foley, C., 2008. EPA Positive Matrix Factorization (PMF) 3.0 Fundamentals & User Guide. Prepared for the US Environmental Protection Agency, Washington, DC, by the National Exposure Research Laboratory, Research Triangle Park.
- Paatero, P., 1997. Least squares formulation of robust non-negative factor analysis. *Chemometrics and Intelligent Laboratory Systems* 37, 23-35.
- Paatero, P., Tapper, U., 1994. Positive Matrix Factorization - A nonnegative factor model with optimal utilization of error-estimates of data values. *Environmetrics* 5, 111-126.
- Riddle, S.G., Robert, M.A., Jakober, C.A., Hannigan, M.P., Kleeman, M.J., 2008. Size-resolved source apportionment of airborne particle mass in a roadside environment. *Environmental Science & Technology* 42, 6580-6586.
- Saudi Network, 2008. Jeddah. <http://www.the-saudi.net/saudi-arabia/jeddah/index.htm>.
- Sofowote, U.M., Hung, H., Rastogi, A.K., Westgate, J.N., Deluca, P.F., Su, Y.S., McCarry, B.E., 2011. Assessing the long-range transport of PAH to a sub-Arctic site using positive matrix factorization and potential source contribution function. *Atmospheric Environment* 45, 967-976.
- Tobiszewski, M., Namiesnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. *Environmental Pollution* 162, 110-119.
- Yamasaki, H., Kuwata, K., Miyamoto, H., 1982. Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons. *Environmental Science & Technology* 16, 189-194.
- Zhang, X.L., Tao, S., Liu, W.X., Yang, Y., Zuo, Q., Liu, S.Z., 2005. Source diagnostics of polycyclic aromatic hydrocarbons based on species ratios: A multimedia approach. *Environmental Science & Technology* 39, 9109-9114.
- Zielinska, B., Sagebiel, J., McDonald, J.D., Whitney, K., Lawson, D.R., 2004. Emission rates and comparative chemical composition from selected in-use diesel and gasoline-fueled vehicles. *Journal of the Air & Waste Management Association* 54, 1138-1150.

499 **TABLE LEGENDS**

500

501 **Table 1.** Average concentrations of PAH in ambient air (vapour and particulate phases) measured
 502 at the three sampling sites. Site A – Zaid Ibn Al-Khatib School, Site B – Al Hgag
 503 School, Site C – Abhor.

504

505 **Table 2.** Average total (vapour and particulate) concentrations of PAH in ambient air measured at
 506 various cities around the world.

507

508

509 **FIGURE LEGENDS**

510

511 **Figure 1.** Map of Jeddah and locations of sampling sites and major PAH stationary sources.

512

513 **Figure 2.** Average particle-vapour partitioning for PAH measured in Jeddah, SA (this study),
 514 Giza, Egypt (Hassan and Khoder, 2012), Assiut, Egypt (Abdallah et al., 2014),
 515 Birmingham, UK (Alam et al., 2013) and Wanqingsha, China (Huang et al., 2014).
 516 Molecular mass increases from left to right.

517

518 **Figure 3.** Source factor profiles of atmospheric PAH obtained from EPA PMF 3.0 model for three
 519 sites in Jeddah, Saudi Arabia. The bars show the chemical profile, and the diamonds
 520 are the variance explained by each factor.

521

522 **Figure 4.** Factor contributions to the three sampling sites and the observed variation between
 523 weekdays and weekends, obtained from EPA PMF 3.0 model.

524

525

526 **Table 1.** Average concentrations of PAH in ambient air (vapour and particulate phases) measured at the three sampling sites. Site A – Zaid Ibn Al-
527 Khatab School, Site B – Al Hgag School, Site C – Abhor.
528

	Average Concentration (ng/m ³)											
	Vapour			Particulate			TOTAL			% Particulate		
	Site A	Site B	Site C	Site A	Site B	Site C	Site A	Site B	Site C	Site A	Site B	Site C
PHE	21.00	16.70	8.60	0.15	0.13	0.05	21.15	16.83	8.65	0.69	0.78	0.53
ANT	1.40	1.60	0.70	0.03	0.03	0.01	1.43	1.63	0.71	2.43	1.66	1.13
FLU	3.30	2.50	1.05	0.17	0.19	0.06	3.47	2.69	1.11	5.00	7.09	5.36
PYR	6.00	3.90	0.75	0.23	0.26	0.07	6.23	4.15	0.82	3.73	6.15	8.34
B(a)A	0.05	0.04	0.02	0.19	0.20	0.05	0.23	0.24	0.06	80.22	84.95	71.31
CHR	0.13	0.05	0.02	0.52	0.56	0.15	0.65	0.61	0.17	79.78	91.34	89.74
B(b)F	0.09	0.07	0.02	0.48	0.40	0.10	0.57	0.47	0.12	83.86	85.02	81.94
B(k)F	0.10	0.06	0.02	0.49	0.36	0.09	0.60	0.42	0.11	82.56	85.85	78.16
B(e)P	0.02	0.02	0.02	0.59	0.47	0.11	0.60	0.50	0.13	97.12	95.30	84.22
B(a)P	0.04	0.03	0.02	0.35	0.27	0.07	0.39	0.30	0.09	89.44	89.79	77.45
IND	0.06	0.02	0.01	0.57	0.44	0.09	0.63	0.47	0.11	91.10	94.85	87.43
D(ah)A	0.07	0.03	BDL	0.08	0.05	0.02	0.15	0.09	0.02	52.48	60.21	100.00
B(ghi)P	0.05	0.03	0.01	1.22	0.99	0.16	1.27	1.03	0.17	95.77	96.83	94.78
COR	BDL	BDL	BDL	0.79	0.61	0.09	0.79	0.61	0.09	100.00	100.00	100.00
Σ ₁₄ PAH	32.31	25.06	11.24	5.85	4.97	1.10	38.17	30.03	12.34	15.33	16.53	8.92

BDL – below detection limit

529

530

531

532

533

534 **Table 2.** Average total (vapour and particulate) concentrations of PAH in ambient air measured at various cities around the world.

		Average total (vapour + particulate) concentrations (ng/m ³)														
		PHE	ANT	FLU	PYR	B(a)A	CHR	B(b)F	B(k)F	B(e)P	B(a)P	IND	D(ah)A	B(ghi)P	COR	Σ ₁₄ PAH
This study	Site A	21.15	1.43	3.47	6.23	0.23	0.65	0.57	0.60	0.60	0.39	0.63	0.15	1.27	0.79	38.17
	Site B	16.83	1.63	2.69	4.15	0.24	0.61	0.47	0.42	0.50	0.30	0.47	0.09	1.03	0.61	30.03
	Site C	8.65	0.71	1.11	0.82	0.06	0.17	0.12	0.11	0.13	0.09	0.11	0.02	0.17	0.09	12.35
Assuit, Egypt ^a		100.39	57.12	79.62	70.04	65.01	78.18	90.26	48.40	-	49.39	32.26	45.86	63.39	-	779.91
Giza, Egypt ^b		257.18	187.27	216.79	188.09	175.99	211.56	229.88	-	-	159.55	123.08	174.97	246.32	-	2,170.68
Tehran, Iran ^c		278.19	155.04	802.78	61.09	30.79	29.41	41.61	27.68	-	18.71	32.28	28.93	34.38	-	1,540.89
Kuwait ^d		2.63	0.24	1.18	1.12	0.35	0.30	0.10	0.09	-	0.25	0.09	0.07	0.15	-	6.57
Wanqingsha, China ^e		40.00	1.54	14.60	9.81	1.09	3.21	3.15	1.29	-	1.65	2.33	0.37	2.67	-	81.71
Zaragoza, Spain ^f		2.30	0.46	1.10	1.10	0.33	0.41	0.47	0.13	0.28	0.29	1.10		1.00	1.50	10.47
Birmingham, UK ^g		20.65	1.61	9.02	10.26	1.15	2.88	0.73	0.53	0.25	0.18	0.22	0.18	0.21	0.15	48.01

^a Abdallah et al. (2014); ^b Hassan and Khoder (2012); ^c Halek et al. (2010); ^d Gevao et al. (2006); ^e Huang et al. (2014); ^f Callen et al. (2008) ^g Alam et al. (2013)

535

536

537

538

540

541 **Figure 1.** Map of Jeddah and locations of sampling sites and major PAH stationary sources.

Figure 2. Average particle-vapour partitioning for PAH measured in Jeddah, SA (this study), Giza, Egypt (Hassan and Khoder, 2012), Assiut, Egypt (Abdallah et al., 2014), Birmingham, UK (Alam et al., 2013) and Wanqingsha, China (Huang et al., 2014). Molecular mass increases from left to right.

Figure 3. Source factor profiles of atmospheric PAH obtained from EPA PMF 3.0 model for three sites in Jeddah, Saudi Arabia. The bars show the chemical profile, and the diamonds are the variance explained by each factor.

Figure 4. Factor contributions to the three sampling sites and the observed variation between weekdays and weekends, obtained from EPA PMF 3.0 model.