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## Influence of Petrochemical Installations Upon PAH Concentrations at Sites in Western Saudi Arabia

Harrison, Roy; Alam, Mohammed; Dang, Juan; Basahi, J; Alghamdi, A.; Ismail, I.M.; Khoder, M.; Hassan, I.A.

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4 **INFLUENCE OF PETROCHEMICAL**  
5 **INSTALLATIONS UPON PAH**  
6 **CONCENTRATIONS AT SITES IN**  
7 **WESTERN SAUDI ARABIA**

8  
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30 **ABSTRACT**

31 Measurements of 16 polycyclic aromatic hydrocarbon (PAH) congeners (particles and vapour) have  
32 been made at three sites over a distance of 230 km on the Red Sea coast of Saudi Arabia. The data  
33 have been pooled with an earlier dataset from three sites in the city of Jeddah, with one urban site  
34 common to both studies. The concentrations and congener profiles are broadly similar for the two  
35 measurement campaigns at the common site. Coefficients of Divergence have been calculated and  
36 show more substantial differences between the sites within the city of Jeddah than are found  
37 between the sites to the north of the city which emphasises the strong concentration gradients within  
38 Jeddah in comparison to those found in the atmosphere of the coastal sites to the north of the city.  
39 A sub-set of data corresponding to days on which the air mass travelled from the northwest parallel  
40 with the Red Sea coast, hence linking the three sites, showed a progressive reduction in  
41 concentrations as the air mass travelled towards the southeast, which is attributed to emissions from  
42 a large source area to the northwest of the sampling sites and either atmospheric dilution or  
43 chemical reaction accounting for a progressive reduction in concentrations with advection of the air  
44 mass. The congener profile is very similar to that identified in earlier work relating to oil refinery  
45 emissions and is consistent with the major petrochemical installation at Yanbu contributing  
46 substantial emissions to the atmosphere which are advected to downwind sites.

47

48 **Keywords:** Polycyclic aromatic hydrocarbons; spatial analyses; atmospheric concentrations;  
49 petrochemical works; Saudi Arabia

50

51 **INTRODUCTION**

52 Polycyclic aromatic hydrocarbons are a group of compounds emitted to the atmosphere from a wide  
53 range of combustion processes. There are many compounds within the group, but conventionally a  
54 small number are commonly analysed – most often the 16 compounds specified by the US  
55 Environmental Protection Agency (Sun et al., 1998). The main driver for measurement is concern  
56 over the health risk posed by the PAH mixture, which is listed by IARC as a Class 1 human  
57 carcinogen (IARC, 2010). Several congeners within the group contribute to that toxicity and  
58 relative potency factors have been proposed by a number of workers (reviewed by Delgado-Saborit  
59 et al., 2011). Both the World Health Organization and the European Commission use  
60 benzo(a)pyrene (BaP) as a marker for the mixture, as this compound typically accounts for a  
61 substantial proportion of the carcinogenic potential of the entire mixture (Delgado-Saborit et al.,  
62 2011). While the WHO publishes slope factors relating cancer risk to exposure concentrations but  
63 no guideline value (WHO, 2000), the European Union has adopted a target value of  $1 \text{ ng m}^{-3}$  of  
64 BaP. A review of the health risk of PAH exposure in the context of indoor air (WHO, 2010) has  
65 highlighted health outcomes other than cancer for which there is strong evidence of a contribution  
66 from PAH. Bae et al. (2010) have shown an association between PAH exposure, measured by a  
67 biomarker, and oxidative stress, which is a precursor to disease. According to Trasande et al.  
68 (2015), children living close to an oil refinery, which was a known source of PAH, showed a  
69 significant increase in symptoms of pre-hypertension. Kim et al. (2013) reviewed the human health  
70 effects of airborne PAH exposure, discussing both acute and chronic health effects.

71

72 As the PAH mixture is a genotoxic carcinogen, there is no wholly safe level of exposure and a  
73 consequent need exists to minimise exposure from all sources. PAH emissions derive from  
74 combustion sources such as gasoline and diesel engine exhaust, wood smoke and food cooking, as  
75 well as from industrial processes such as steel production and anode baking in aluminium  
76 production, and from the evaporation of fossil fuels (Baek et al., 1991; Mastral and Callen, 2000).

77 Since the development of cost-effective abatement strategies requires a sound knowledge of  
78 individual source contributions to ambient concentrations, there is a pressing need for source  
79 apportionment studies, such as that conducted by Jang et al. (2013) using data from the United  
80 Kingdom PAH monitoring network and Wang et al. (2015) using a large dataset collected at a  
81 megacity in China. In addition to the application of Positive Matrix Factorization to a multi-site,  
82 multicomponent dataset, Jang et al. (2013) used spatial distribution analysis to infer source  
83 contributions. The differences in concentrations between paired sites were used to infer source  
84 contributions, which could be compared with emissions inventory data. Site pairs included  
85 roadside/urban background pairs and industrial/urban background pairs of sites. Mari et al. (2010)  
86 also made a qualitative comparison of congener profiles between urban and rural sites, and  
87 compared a road traffic profile with an urban background concentration profile, but did not use  
88 quantitative measures of difference.

89

90 A factor to consider in analysing ambient air measurements of PAH is that the compounds are  
91 reactive in the atmosphere at differing rates leading to degradation, and a consequent change occurs  
92 in the ratios of compounds from those emitted at source (Keyte et al., 2013). A further  
93 consideration is that PAH are semi-volatile compounds which actively partition between the vapour  
94 and condensed phases, and to fully understand their airborne concentrations it is necessary to  
95 measure both phases (Yamasaki et al., 1982). Receptor modelling is also likely to generate  
96 misleading results unless the sum of both phases is used in the model (Harrison et al., 1996; Xie et  
97 al., 2013; Gao et al., 2015).

98

99 There have been relatively few measurements of PAH in countries from the Middle Eastern region.  
100 Alghamdi et al. (2015a) review data from Assiut, Egypt (Abdallah and Atia, 2014), Giza, Egypt  
101 (Hassan and Khoder, 2012), Tehran, Iran (Halek et al., 2010), Kuwait (Gevao et al., 2006) and  
102 Zonguldak, Turkey (Akyuz and Cabuk, 2010) as well as measurements from two locations in Saudi

103 Arabia: Makkah (Habebullah, 2013) and Riyadh (El-Mubarek et al., 2014). These show a huge  
104 diversity in concentrations, with concentrations reported from Egypt and Iran far exceeding those  
105 from sites in Jeddah, Saudi Arabia (measured by Alghamdi et al., 2015a), and those from Kuwait  
106 falling below the Jeddah data. Both the studies of Habebullah (2013) and El-Mubarak et al. (2014)  
107 report very high PAH concentrations; the latter reported average benzo(a)pyrene of  $400 \text{ ng m}^{-3}$ ,  
108 which is so high as to require independent confirmation. Due to the very different climate, and  
109 availability of fuels, it is anticipated that PAH sources may be very different in the Middle Eastern  
110 region from that in temperate western countries. It is anticipated that there would be little use of  
111 coal or wood as fuels, but greater dependence upon petroleum-based products.

112

113 The anticipated dominance of petroleum based sources is borne out by a receptor modelling study  
114 conducted in Saudi Arabia. In a study of PAH measured at three sites in Jeddah, Saudi Arabia,  
115 Alghamdi et al. (2015a) used PMF to apportion PAH to three factors representing traffic emissions,  
116 industrial sources, especially an oil refinery, and oil combustion. The purpose of this research is to  
117 extend the geographic coverage of PAH concentrations and source attribution well beyond Jeddah  
118 and Riyadh for which data are already available into that part of the western coast which contains  
119 extensive petrochemical industry activity. In this paper we report further measurements from one  
120 of the sites used by Alghamdi et al. (2015a) – Site C in that paper – and over the same campaign  
121 period from two further sites up to 230 km to the north of Jeddah. These new data include  
122 measurements from two sites which substantially increase the spatial coverage, and were collected  
123 so as to test for spatial trends in concentration within the prevailing air mass movements from  
124 north-west towards south-east along the Red Sea coast (see Figure 1). They also include a rural site  
125 for which very few data are available in this region.

126

127

128

129 **EXPERIMENTAL**

130 **Sampling Sites**

131 These are shown in Figure 1.

132

133 **FIGURE 1 HERE**

134

135 **Site A (Refinery) (21.4439°N; 39.2005°E)** is a primary school situated in a highly populated  
136 economically disadvantaged residential area in the south of the city of Jeddah, about 700 metres  
137 east of the Jeddah oil refinery, and close to the Port of Jeddah.

138

139 **Site B (Ring Road) (21.4727°N; 39.2755 °E)** is also a primary school in the eastern part of Jeddah,  
140 about 150 metres from the heavily trafficked Al-Haramian ring road.

141

142 **Site C (Abhur) (21.7572°N; 39.1147°E)** is located in the grounds of a research institute on the Red  
143 Sea coast to the west of major roads. It is in the northern suburbs of the major city of Jeddah  
144 (population 5 million), with the King Abdulaziz international airport to the east (inland). The site is  
145 approximately 130 km to the SE of Rabegh.

146

147 **Site D (Rabegh) (22.8122°N; 39.0664°E)** is a site located about 1 km from the residential areas of  
148 this substantial city, which has appreciable local industry. The sampling site is ca. 500 metres east  
149 of the coastal road. It is approximately 100 km SSE of Rayes.

150

151 **Site E (Rayes) (23.5756°N; 38.6058°E)** is a sparsely developed area with little road traffic and no  
152 appreciable local sources. The sampling site is located about 950 metres inland (east) of the coastal  
153 road, and 25-50 km SSE of the large industrial complex in the region of Yanbu.

154



155 Wind trajectories in western Saudi Arabia often travel parallel to the coast from an approximately  
156 north-westerly direction. Consequently, three sites were selected for air sampling spaced along the  
157 coast, to the south east of the major petrochemical plant located south of Yanbu. Thus, air masses  
158 travelling parallel to the coast after Yanbu would firstly cross the site at Rayes, some 25-50 km  
159 southeast of the industrial activities around Yanbu (see Figure 1). Rayes is in a sparsely developed  
160 area and would be expected to experience predominantly regionally polluted air masses, as well as  
161 possibly being influenced by emissions from the Yanbu industrial complex. The second site along  
162 the coast is Rabegh which is located within a major urban area, with both local road traffic and  
163 industrial influences. It is 100 km from Rayes. The third site, Abhur is in the northern suburbs of  
164 Jeddah city, about 130 km from Rabegh. Southerly air masses would carry the pollution load from  
165 the city, while air masses following the coast from the north-west would cross few areas of  
166 population between Rabegh and Abhur. The area is mainly residential with local traffic influences,  
167 but no industry, other than that to the south within Jeddah. The city of Jeddah has both high traffic  
168 density and major fixed emission sources including an oil refinery and a desalination plant which  
169 burns fuel oil.

170

171 In order to carry out an effective Lagrangian test of compositional change, the sampling of air  
172 masses at Sites E, D and C was staggered to allow for the atmospheric transport of air masses.  
173 Samples were hence initiated sequentially at 05.00 (Site E), 11.00 (Site D) and 17.00 (Site C) local  
174 time, and each continued for 24 hours.

175

### 176 **Dates of Sampling**

177 The first campaign was at Sites A, B and C, and daily 24-hour samples were collected  
178 simultaneously at all sites between 23 February 2013 and 23 April 2013. Peak daily temperatures  
179 over this period ranged from 26 to 30°C. The data from that campaign have been reported as part of  
180 a study of brachial artery distensibility in relation to pollutant exposure by Trasande et al. (2015), a

181 receptor modelling study by Alghamdi et al. (2015a), and a study of urinary PAH metabolites by  
182 Alghamdi et al. (2015b). The second campaign took place at Sites C, D and E from 16 June 2013 to  
183 7 July 2013 and 17 September to 1 October 2013 (summer) and 23 December 2013 to 30 January  
184 2014 (winter). Peak hourly temperatures ranged from 38-47°C (summer) and 23-30°C (winter).

185

### 186 **Sampling Instruments**

187 Samples were collected using a “pesticide” sampler (TE-PUF, Tisch Environmental Inc.) which  
188 draws air (240-300 m<sup>3</sup> per day) through a TSP inlet onto a quartz microfibre filter (TE-QMA4;  
189 10.16 cm) to collect particulate matter, followed by an adsorbent polyurethane (PUF) substrate to  
190 collect vapour phase compounds.

191

### 192 **Chemical Analysis**

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

201

202 Samples were analysed for 16 PAH using the methodology described previously (Delgado-Saborit  
203 et al., 2010; 2013). Briefly, filter and PUF substrates were spiked with 1000 pg  $\mu\text{L}^{-1}$  deuterated  
204 internal standards for quantification. Nine deuterated compounds were used, covering the volatility  
205 range from acenaphthylene-d<sub>8</sub> to benzo(ghi)perylene-d<sub>12</sub>. A recovery standard, p-terphenyl-d<sub>14</sub> was  
206 also added using a solution of 2000 pg  $\mu\text{L}^{-1}$ . Filters were immersed in dichloromethane (DCM) and

207 ultrasonicated for 15 min at 20°C. The extract was subsequently dried and cleaned using a  
208 chromatography column filled with 0.5 g of anhydrous sodium sulphate (puriss grade for HPLC).  
209 The extract was further concentrated to 50 µL under a gentle N<sub>2</sub> flow. PUF substrates were  
210 immersed in 100 mL of DCM and ultrasonicated for 20 min at 20°C. The sample was then  
211 concentrated to 10 mL using N<sub>2</sub> and subsequently dried and cleaned as outlined for the filters  
212 above.

213

214 Samples were analysed for PAH compounds using Gas Chromatography (6890, Agilent  
215 Technologies) equipped with a non-polar capillary column (Agilent HP-5MS, 30 m, 0.25 mm ID,  
216 0.25 µm film thickness — 5% phenylpolysiloxane) in tandem with a Mass Spectrometer (5973 N,  
217 Agilent Technologies). The precision of analysis was 8±4% (range: RSD, 0.3-9.7%) and the  
218 accuracy, expressed as the difference between the measured and true value as a percentage of the  
219 true value was 6±4% (range: -6 to 25%). The analytical detection limits varied widely between  
220 congeners, and sample detection limits estimated from analysis of blank filters and PUFs all lay  
221 well below 1 pg m<sup>-3</sup> for the 24-hour air samples. Further information regarding the analytical  
222 procedure can be found in Delgado-Saborit et al. (2010; 2013). Some of the PUF substrates  
223 showed contamination in the later part of the chromatogram making quantification of compounds  
224 from benzo(e)pyrene to coronene unreliable. As these compounds are typically > 90% particulate  
225 (Alghamdi et al, 2015a) the vapour component has not been quantified, therefore implying an  
226 underestimation of up to 10% in concentration of these compounds.

227

## 228 **RESULTS AND DISCUSSION**

229 Mean concentrations of PAH for each congener and each site appear in Table 1, and  
230 diagrammatically in Figure 2. Phase partitioning was considered in detail in our earlier study  
231 (Alghamdi et al., 2015a), and was found to be similar in this dataset. The bars marked Site A, B and  
232 C in Figure 2 derive from data from the first campaign, while the data for Rayes (site E), Rabegh

233 (site D) and Abhur (site C2) are from the second campaign. This shows a clear spatial pattern, with  
234 highest concentrations at Site A which is strongly influenced by the Jeddah refinery and port, and  
235 second highest at Site B where the main influence is from road traffic. Concentrations at Site C,  
236 Abhur on the northern boundaries of Jeddah, can be compared between the first and second  
237 campaign. It can be seen from Figure 2 that concentrations at the Abhur site (C1 and C2) were  
238 broadly similar in the two campaigns.

239

240 There are indications in Figure 2 of a concentration gradient in the sense of Rayes (Site E) >  
241 Rabegh (Site D) > Abhur (Site C). This was explored further by selecting a sub-set of data  
242 corresponding only to those days when the air mass back trajectory ran from north-west to south-  
243 east parallel to the Red Sea coast of Saudi Arabia, as in the example trajectory shown in Figure 3.  
244 This sub-set corresponds to a total of 14 samples which included all 12 from the summer campaign  
245 and 2 from the winter campaign measurements. When averaged (Figure 4), these show a marked  
246 gradient in most PAH congeners from Site E (Rayes) > Site D (Rabegh) > Site C (Abhur). This is  
247 despite the different characteristics of the sites and the fact that Rabegh may have local source  
248 influences, and Abhur is in an area with light local urban traffic. The fact that the highest  
249 concentrations are observed at remote Site E (Rayes) is clearly indicative of a major source to the  
250 north-west of that site, which is presumably the major petrochemical complex at Yanbu. As the air  
251 mass is advected along the Red Sea coastline towards the south-east, concentrations are reduced  
252 progressively through atmospheric dispersion/dilution processes and chemical reactions of the PAH  
253 (Keyte et al., 2013).

254

255 TABLE 1 HERE

256

257 FIGURE 2, 3 AND 4 HERE

258

259 The Coefficient of Divergence is defined as:

$$COD_{fh} = \sqrt{\frac{1}{n} \sum_{i=1}^n \left( \frac{x_{if} - x_{ih}}{x_{if} + x_{ih}} \right)^2}$$

260 In which  $x_{if}$  and  $x_{ih}$  are the respective concentrations for sampling period  $i$  at sites  $f$  and  $h$   
261 respectively and  $n$  is the number of observations. Values of COD for the site pairs measured  
262 simultaneously in this study appear in Table 2. Small values of COD are indicative of only small  
263 differences in concentrations between sites, while values approaching the theoretical maximum of  
264 one reflect large inter-site differences. Comparisons are based upon total (particulate plus vapour)  
265 concentrations.

266

267 Data from the first campaign appear in Table 2(a), and show a large divergence between both Site  
268 A, close to the Jeddah refinery, and Site B, close to the major highway, and Site C in the relatively  
269 unpolluted northern suburbs. Differences between the more polluted Sites A and B are much  
270 smaller. With respect to the second campaign and the three more northerly sites, COD values are  
271 typically intermediate. The lowest values, representing the greatest similarity between sites are  
272 between Site D (Rabegh) and Site C (Abhur). Not unexpectedly, the largest differences are seen  
273 between Sites E and C which have the largest spatial separation.

274

275 TABLE 2 HERE

276

277 One sample, collected on 29 September 2013 showed a major elevation in concentrations of all  
278 PAH. This was seen both in the particulate and vapour forms, and hence it is considered to reflect a  
279 genuine atmospheric phenomenon, and not laboratory contamination of a single sample. It is  
280 thought likely to be the result of a single major contribution event close to the Rayes sampling site  
281 (E), which showed the greatest elevation in concentrations. For many of the congeners, a lesser  
282 elevation was seen on the same sampling date at the downwind Rabegh sampling site. The same

283 general pattern of concentrations at Rayes (site E) > Rabegh (site D) > Abhur (site C) was repeated  
284 in this sample, and it has been retained in the averaging process as it does not affect the overall  
285 pattern of absolute or relative concentrations appreciably.

286

287 Diagnostic ratios are widely used in source attribution of PAH, although where multiple sources are  
288 present, their use is extremely limited (Galarneau, 2008). Diagnostic ratios are also influenced by  
289 atmospheric degradation processes (Tobiszewski and Namiesnik, 2012). There appear to be very  
290 few published data concerning PAH from petrochemical complexes, but Zhao et al. (2015) report  
291 data from eight villages surrounding a large petrochemical complex in Guangzhou, China. They  
292 report that ratios of ANT/(ANT + PHE) which fall below 0.1 are typical of a petrogenic source such  
293 as a petrochemical works and their data showed ratios within this range. They cite Ravindra et al.  
294 (2008) as the source of this information but that paper does not appear to refer to petrochemical  
295 sources. There is however support for this ratio to distinguish petrogenic from pyrogenic sources of  
296 PAH in the work of Yunker et al. (2002) and Pies et al. (2008). In a recent paper, Dominguez-  
297 Morueco et al. (2015) report PAH concentrations measured with passive air samplers in the  
298 petrochemical area of Tarragona, Spain. They report a predominance of 3-ring compounds and  
299 ratios of ANT/(ANT+PHE) of <0.1. It is notable that ratios of ANT/(ANT + PHE) fell below 0.1 at  
300 all of the measurements sites used in our study. This is unsurprising for the sites in Jeddah where  
301 there is a petroleum refinery within the boundaries of the city, and Site A was located close to it.  
302 The fact that the ratios fell well below 0.1 at the Rayes site, which is downwind of the  
303 petrochemical complex at Yanbu is strongly suggestive of the petrochemical complex being the  
304 source of the elevated PAH concentrations at Rayes. Alternatively, because of the greater chemical  
305 reactivity of anthracene relative to phenanthrene, it may simply be due to degradation of anthracene  
306 during air mass transport. Alam et al. (2013) examined ANT/(ANT + PHE) ratios from two sites in  
307 Birmingham, UK, one located at roadside and the other at urban background and also calculated a  
308 traffic increment from the difference in concentration between the sites. They examined diagnostic

309 ratios and report values for  $ANT/(ANT + PHE)$  which are all in excess of 0.1 for the traffic  
310 increment. The majority are in excess of 0.1 for the roadside site, but all of the values of this ratio  
311 fall below 0.1 for the urban background site which they interpret as due to the atmospheric  
312 reactivity of anthracene being greater than phenanthrene and reducing the ratio as the air ages.  
313 Consequently, we feel that diagnostic ratios do not give us a definitive indication of the sources of  
314 elevated concentrations of PAH at Rayes but that the elevation is consistent with a petrogenic  
315 source such as the petrochemical complex upwind at Yanbu.

316

317 There were insufficient samples to carry out a further PMF analysis from the second campaign.  
318 However, the congener profile of the PAH can be compared with those of the three source-related  
319 factors identified by Alghamdi et al. (2015a). The industrial (oil refinery) factor has substantial  
320 concentrations of phenanthrene > pyrene > fluoranthene > anthracene with only very minor  
321 amounts of other congeners. This is very similar to the profile seen in Figure 4 for the three sites  
322 during the second campaign, when winds were parallel to the coast.

323

## 324 **CONCLUSIONS**

325 The results of the Coefficients of Divergence calculations show strong gradients in concentration  
326 between the heavily polluted sites in southern Jeddah and the background site (Site C, Abhur) in the  
327 northern suburbs of the city. This is consistent with conclusions in our earlier work that Sites A and  
328 B in the south of Jeddah were heavily influenced by local sources, a refinery and a major highway  
329 respectively. Concentration gradients between the sites on the Red Sea coast to the north of Jeddah  
330 generate much smaller Coefficients of Divergence indicative of lesser concentration gradients. The  
331 steady decline seen in Figure 4 for those days in which the air mass moved from northwest,  
332 southeast along the Red Sea coast are consistent with a major source of PAH to the north of the  
333 Rayes sampling site. The congener profile is consistent with that source being the large  
334 petrochemical works in the vicinity of Yanbu. Figure 4 also shows a steady decline in

335 concentrations as the air mass moves towards the southeast which might be attributable either to  
336 progressive dilution with cleaner air or alternatively to reduction in concentrations due to chemical  
337 reactions. Without further supporting information, it is not possible to clearly identify the causal  
338 factor. Such supporting information might include measurements of a passive (unreactive) tracer  
339 compound from which to assess the extent of dilution during transport.

340

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489

490 **TABLE LEGENDS**

491  
492 **Table 1:** Total concentrations of PAH congeners at all sites ( $\text{ng m}^{-3}$ )

493  
494 **Table 2:** (a) Coefficients of Divergence (COD) values for total PAH for sites A, B and C1  
495 (first campaign); (b) COD values for total PAH for sites D, E and C2 (second  
496 campaign).

497  
498  
499 **FIGURE LEGENDS**

500  
501 **Figure 1:** Locations of sampling sites and the city of Jeddah. The sites are: A-refinery; B-ring  
502 road; C-Abhur; D-Rabegh and E-Rayes.

503  
504 **Figure 2:** Average congener profile of PAH from both sampling campaigns at the five sites,  
505 including both campaign data for Site C.

506  
507 **Figure 3:** Air mass back trajectories to the the three sites for 17 September 2013 ending at 950  
508 mb showing the air mass running parallel to the Red Sea coast.

509  
510 **Figure 4:** Average congener profile of PAH from the second sampling campaign including  
511 only air samples when the air mass travelled from north-west to south-east parallel to  
512 the Red Sea coast.

513

**Table 1:** Total concentrations of PAH congeners at all sites (ng m<sup>-3</sup>).

Congener	Site A		Site B		Site C1		Site C2		Site D		Site E	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Fluorene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.47	0.20-1.54	0.90	0.45-1.92	1.13	0.36-6.98
Phenanthrene	21.15	11.63-41.55	16.83	5.75-29.67	8.65	2.71-21.91	6.03	2.57-12.09	7.97	4.51-14.41	9.58	3.24-29.92
Anthracene	1.43	0.40-4.14	1.63	0.57-3.13	0.71	0.17-1.65	0.31	0.14-0.79	0.46	0.20-1.30	0.82	0.19-7.53
Fluoranthene	3.47	1.01-7.77	2.69	1.22-4.79	1.11	0.40-2.42	0.94	0.50-1.67	1.23	0.69-2.53	1.18	0.40-5.86
Pyrene	6.23	1.43-15.30	4.15	1.85-8.06	0.82	0.32-1.44	0.89	0.43-1.50	1.45	0.79-2.51	1.11	0.27-7.08
Retene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.56	0.05-1.14	0.47	0.16-1.09	0.52	0.21-1.75
Benzo(a)anthracene	0.23	0.07-0.79	0.24	0.08-0.33	0.06	0.02-0.23	0.26	0.05-0.59	0.37	0.04-1.00	0.37	0.02-1.48
Chrysene	0.65	0.20-2.27	0.61	0.26-1.03	0.17	0.06-0.60	0.26	0.07-0.47	0.28	0.02-0.61	0.39	0.06-1.91
Benzo(b)fluoranthene	0.57	0.17-1.11	0.47	0.22-0.81	0.12	0.03-0.42	0.12	0.01-0.25	0.16	0.05-0.25	0.23	0.04-1.53
Benzo(k)fluoranthene	0.60	0.19-1.24	0.42	0.23-0.71	0.11	0.03-0.37	0.12	0.02-0.23	0.15	0.02-0.25	0.24	0.04-2.08
Benzo(e)pyrene	0.60	0.17-1.30	0.50	0.24-0.82	0.13	0.04-0.42	0.10	0.01-0.27	0.11	0.02-0.29	0.19	0.03-1.68
Benzo(a)pyrene	0.39	0.09-1.01	0.30	0.12-0.56	0.09	0.02-0.30	0.07	0.00-0.16	0.09	0.01-0.14	0.16	0.01-1.53
Indeno(1,2,3-cd)pyrene	0.63	0.22-1.21	0.47	0.26-0.75	0.11	0.02-0.38	0.09	0.01-0.17	0.09	0.02-0.29	0.18	0.03-1.89
Dibenz(a,h)anthracene	0.15	0.04-0.27	0.09	0.04-0.14	0.02	0.01-0.07	0.03	0.00-0.08	0.04	0.01-0.12	0.08	0.01-0.67
Benzo(ghi)perylene	1.27	0.46-2.38	1.03	0.51-1.61	0.17	0.03-0.64	0.11	0.02-0.32	0.18	0.04-0.69	0.24	0.04-2.32
Coronene	0.79	0.29-1.59	0.61	0.32-0.88	0.09	0.01-0.36	0.09	0.03-0.21	0.16	0.04-0.45	0.20	0.06-1.54

Note : Sites A, B and C1 refer to the first campaign (Alghamdi et al. 2015a). Sites C2 (Abhur), D (Raybegh) and E (Rayes) refer to the second campaign.

: n.d. = not determined

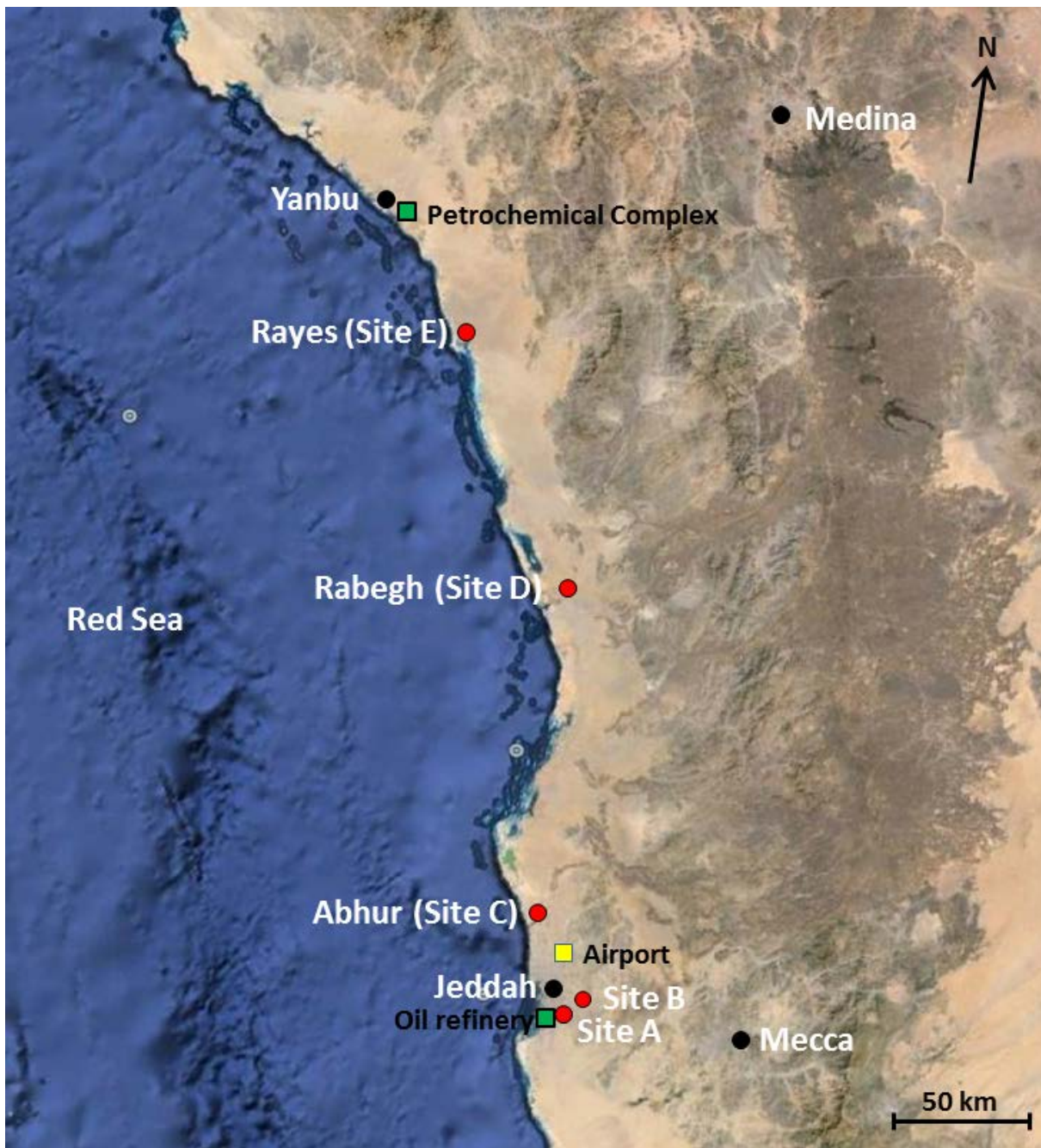
**Table 2:** (a) Coefficients of Divergence (COD) values for total PAH congeners for sites A, B and C1 (first campaign); (b) COD values for total PAH for sites C2, D and E (second campaign).

(a)

Species	COD <sub>A&amp;B</sub>	COD <sub>A&amp;C1</sub>	COD <sub>B&amp;C1</sub>
Phenanthrene	0.250	0.459	0.433
Anthracene	0.313	0.464	0.518
Fluoranthene	0.374	0.543	0.493
Pyrene	0.406	0.728	0.676
Benzo(a)anthracene	0.399	0.611	0.691
Chrysene	0.348	0.607	0.654
Benzo(b)fluoranthene	0.227	0.685	0.674
Benzo(k)fluoranthene	0.272	0.724	0.677
Benzo(e)pyrene	0.269	0.671	0.680
Benzo(a)pyrene	0.296	0.675	0.677
Indeno(1,2,3-cd)pyrene	0.237	0.749	0.723
Dibenz(a,h)anthracene	0.356	0.769	0.677
Benzo(ghi)perylene	0.227	0.806	0.793
Coronene	0.238	0.828	0.810

(b)

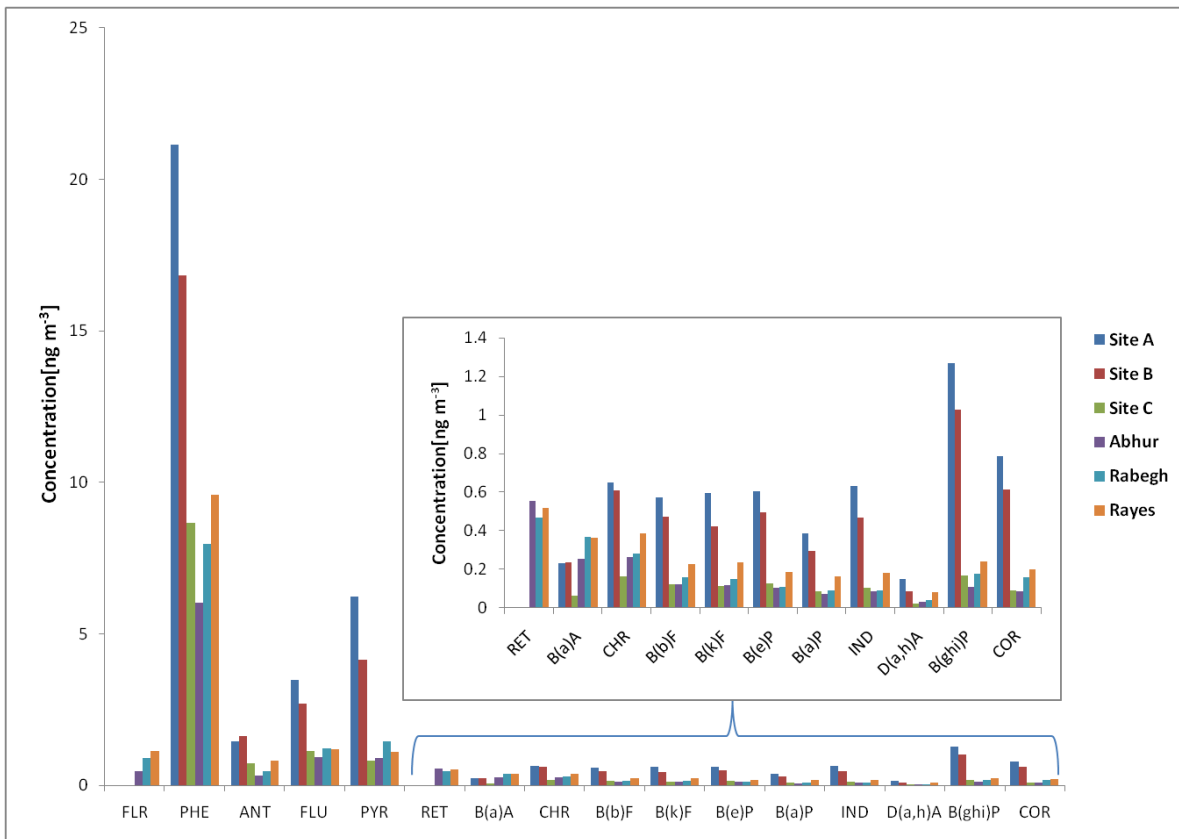
Species	COD <sub>C2&amp;D</sub>	COD <sub>C2&amp;E</sub>	COD <sub>D&amp;E</sub>
Fluorene	0.430	0.398	0.314
Phenanthrene	0.250	0.474	0.253
Anthracene	0.261	0.413	0.316
Fluoranthene	0.188	0.456	0.361
Pyrene	0.291	0.480	0.447
Benzo(a)anthracene	0.414	0.471	0.342
Chrysene	0.485	0.558	0.453
Retene	0.292	0.402	0.331
Benzo(b)fluoranthene	0.155	0.305	0.374
Benzo(k)fluoranthene	0.196	0.388	0.387
Benzo(e)pyrene	0.287	0.465	0.370
Benzo(a)pyrene	0.320	0.472	0.332
Indeno(1,2,3-cd)pyrene	0.273	0.468	0.385
Dibenz(a,h)anthracene	0.364	0.564	0.408
Benzo(ghi)perylene	0.376	0.482	0.353
Coronene	0.363	0.462	0.333



1

2 **Figure 1:** Locations of sampling sites and the city of Jeddah. The sites are: A-refinery; B-ring  
 3 road; C-Abhur; D-Rabegh and E-Rayes.

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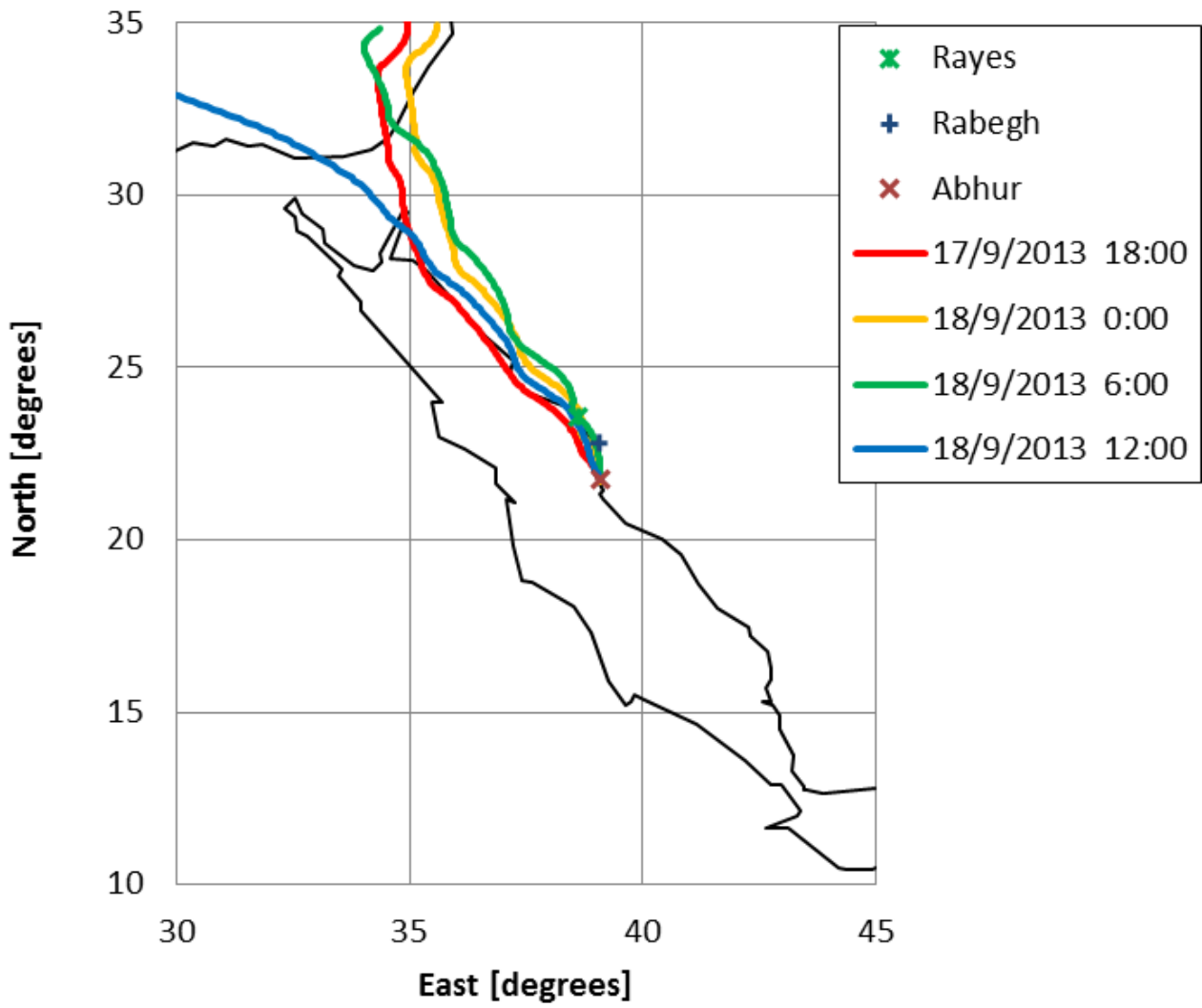
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6 **Figure 2:** Average congener profile of PAH from both sampling campaigns at the five sites,  
 7 including both campaign data for Site C. The site C data refer to the first campaign (1) and the  
 8 Abhur data refer to the second campaign (2).  
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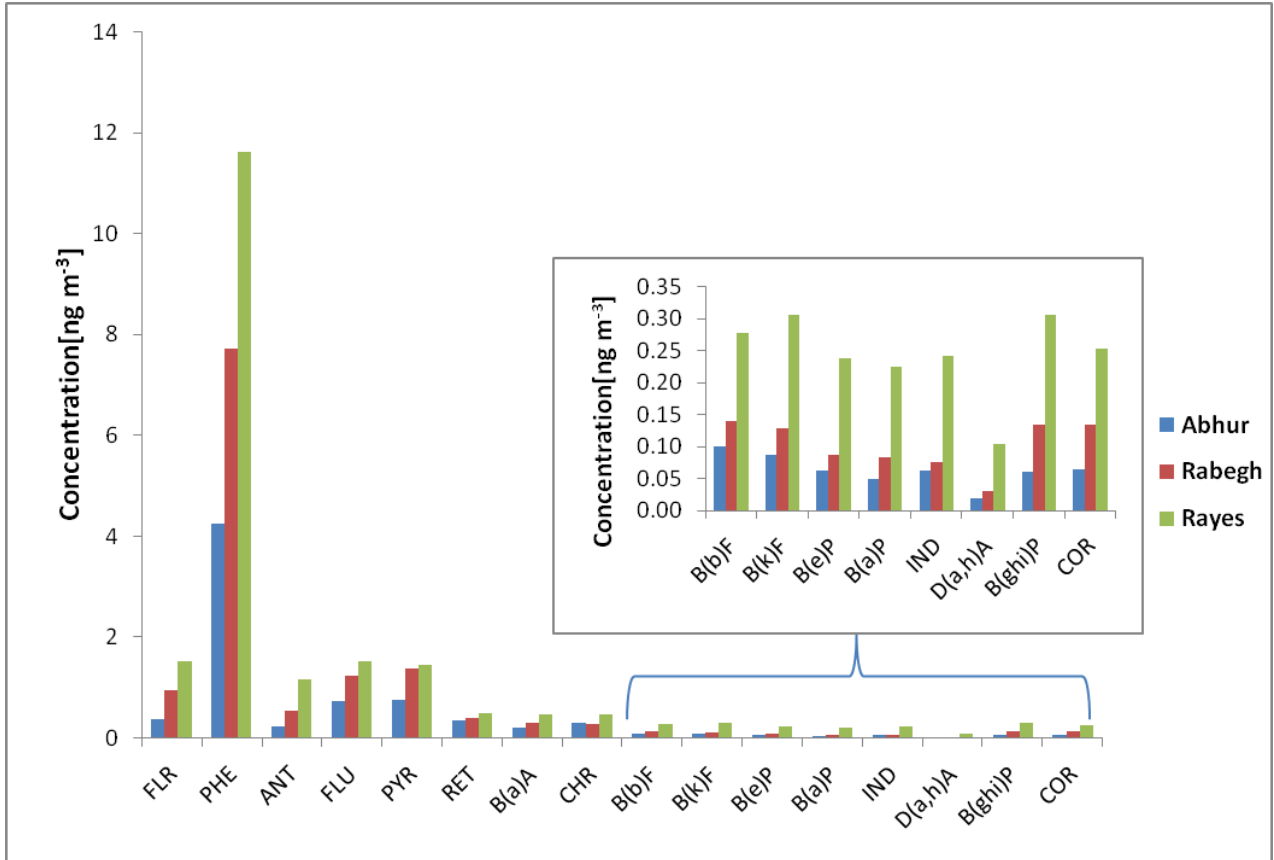
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13 **Figure 3:** Air mass back trajectories to the the three sites for 17 September 2013 ending at 950 mb  
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17

18 **Figure 4:** Average congener profile of PAH from the second sampling campaign including only air  
 19 samples when the air mass travelled from north-west to south-east parallel to the Red Sea coast.  
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