UNIVERSITY OF BIRMINGHAM
University of Birmingham Research at Birmingham

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.

DOI:
10.1016/j.apr.2016.05.012

License:
Creative Commons: Attribution-NonCommercial-NoDerivs (CC BY-NC-ND)

Document Version
Peer reviewed version

Citation for published version (Harvard):
Harrison, R, Alam, M, Dang, J, Basahi, J, Alghamdi, A, Ismail, IM, Khoder, M & Hassan, IA 2016, 'Influence of Petrochemical Installations Upon PAH Concentrations at Sites in Western Saudi Arabia', *Atmospheric Pollution Research*. https://doi.org/10.1016/j.apr.2016.05.012

Link to publication on Research at Birmingham portal

Publisher Rights Statement:
Checked 13/07/2016

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.

Download date: 19. Apr. 2024

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.

Document Version
Peer reviewed version

Citation for published version (Harvard):
Harrison, R, Alam, M, Dang, J, Basahi, J, Alghamdi, A, Ismail, IM, Khoder, M & Hassan, IA 2016, 'Influence of Petrochemical Installations Upon PAH Concentrations at Sites in Western Saudi Arabia' Atmospheric Pollution Research.

INFLUENCE OF PETROCHEMICAL INSTALLATIONS UPON PAH CONCENTRATIONS AT SITES IN WESTERN SAUDI ARABIA

Roy M. Harrison[1,2,3*], Mohammed S. Alam[1], Juan Dang[1‡],
J. Basahi[2], Mansour A. Alghamdi[3], I.M. Ismail[2], M. Khoder[2,3]
and I.A. Hassan[2,4]

(r.m.harrison@bham.ac.uk; m.s.alam@bham.ac.uk; JXD507@bham.ac.uk;
djsdu2012@126.com; jbasahi@kau.edu.sa; mans99@gmail.com;
iqbal30@hotmail.com; khoder_55@yahoo.com; ihassan_eg@yahoo.com)

[1]School of Geography, Earth and Environmental Sciences
University of Birmingham, Edgbaston, Birmingham, B15 2TT
United Kingdom

[2]Center of Excellence in Environmental Studies, King Abdulaziz
University, Jeddah, 21589, Saudi Arabia

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

[4]Faculty of Science, Alexandria University
21526 El Shatby, Alexandria, Egypt

[‡] Also at: Environment Research Institute, Shandong University, Jinan 250100, P.R. China

[*] To whom correspondence should be addressed
Tele: +44 121 414 3494; Fax: +44 121 414 3708; Email: r.m.harrison@bham.ac.uk

ABSTRACT

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

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

INTRODUCTION

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

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

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

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

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

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

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

EXPERIMENTAL

Sampling Sites

These are shown in Figure 1.

FIGURE 1 HERE

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

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

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

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

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

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

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

Dates of Sampling

The first campaign was at Sites A, B and C, and daily 24-hour samples were collected simultaneously at all sites between 23 February 2013 and 23 April 2013. Peak daily temperatures over this period ranged from 26 to 30ºC. The data from that campaign have been reported as part of a study of brachial artery distensibility in relation to pollutant exposure by Trasande et al. (2015), a receptor modelling study by Alghamdi et al. (2015a), and a study of urinary PAH metabolites by Alghamdi et al. (2015b). The second campaign took place at Sites C, D and E from 16 June 2013 to 7 July 2013 and 17 September to 1 October 2013 (summer) and 23 December 2013 to 30 January 2014 (winter). Peak hourly temperatures ranged from 38-47ºC (summer) and 23-30ºC (winter).

Sampling Instruments

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

Chemical Analysis

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

Samples were analysed for 16 PAH using the methodology described previously (Delgado-Saborit et al., 2010; 2013). Briefly, filter and PUF substrates were spiked with 1000 pg μL^{-1} deuterated internal standards for quantification. Nine deuterated compounds were used, covering the volatility range from acenaphthylene-d_8 to benzo(ghi)perylene-d_{12}. A recovery standard, p-terphenyl-d_{14} was also added using a solution of 2000 pg μL^{-1}. Filters were immersed in dichloromethane (DCM) and ultrasonicated for 15 min at 20ºC. The extract was subsequently dried and cleaned using a chromatography column filled with 0.5 g of anhydrous sodium sulphate (puriss grade for HPLC). The extract was further concentrated to 50 µL under a gentle N_2 flow. PUF substrates were immersed in 100 mL of DCM and ultrasonicated for 20 min at 20ºC. The sample was then concentrated to 10 mL using N_2 and subsequently dried and cleaned as outlined for the filters above.

Samples were analysed for PAH compounds using Gas Chromatography (6890, Agilent Technologies) equipped with a non-polar capillary column (Agilent HP-5MS, 30 m, 0.25 mm ID, 0.25 µm film thickness — 5% phenylpolysiloxane) in tandem with a Mass Spectrometer (5973 N, Agilent Technologies). The precision of analysis was 8±4% (range: RSD, 0.3-9.7%) and the accuracy, expressed as the difference between the measured and true value as a percentage of the true value was 6±4% (range: -6 to 25%). The analytical 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. (2010; 2013). Some of the PUF substrates showed contamination in the later part of the chromatogram making quantification of compounds from benzo(e)pyrene to coronene unreliable. As these compounds are typically > 90% particulate (Alghamdi et al, 2015a) the vapour component has not been quantified, therefore implying an underestimation of up to 10% in concentration of these compounds.

RESULTS AND DISCUSSION

Mean concentrations of PAH for each congener and each site appear in Table 1, and diagrammatically in Figure 2. Phase partitioning was considered in detail in our earlier study (Alghamdi et al., 2015a), and was found to be similar in this dataset. The bars marked Site A, B and C in Figure 2 derive from data from the first campaign, while the data for Rayes (site E), Rabegh (site D) and Abhur (site C2) are from the second campaign. This shows a clear spatial pattern, with highest concentrations at Site A which is strongly influenced by the Jeddah refinery and port, and second highest at Site B where the main influence is from road traffic. Concentrations at Site C, Abhur on the northern boundaries of Jeddah, can be compared between the first and second campaign. It can be seen from Figure 2 that concentrations at the Abhur site (C1 and C2) were broadly similar in the two campaigns.

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

TABLE 1 HERE

FIGURE 2, 3 AND 4 HERE

The Coefficient of Divergence is defined as:

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

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

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

TABLE 2 HERE

One sample, collected on 29 September 2013 showed a major elevation in concentrations of all PAH. This was seen both in the particulate and vapour forms, and hence it is considered to reflect a genuine atmospheric phenomenon, and not laboratory contamination of a single sample. It is thought likely to be the result of a single major contribution event close to the Rayes sampling site (E), which showed the greatest elevation in concentrations. For many of the congeners, a lesser elevation was seen on the same sampling date at the downwind Rabegh sampling site. The same general pattern of concentrations at Rayes (site E) > Rabegh (site D) > Abhur (site C) was repeated in this sample, and it has been retained in the averaging process as it does not affect the overall pattern of absolute or relative concentrations appreciably.

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

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

CONCLUSIONS

The results of the Coefficients of Divergence calculations show strong gradients in concentration between the heavily polluted sites in southern Jeddah and the background site (Site C, Abhur) in the northern suburbs of the city. This is consistent with conclusions in our earlier work that Sites A and B in the south of Jeddah were heavily influenced by local sources, a refinery and a major highway respectively. Concentration gradients between the sites on the Red Sea coast to the north of Jeddah generate much smaller Coefficients of Divergence indicative of lesser concentration gradients. The steady decline seen in Figure 4 for those days in which the air mass moved from northwest, southeast along the Red Sea coast are consistent with a major source of PAH to the north of the Rayes sampling site. The congener profile is consistent with that source being the large petrochemical works in the vicinity of Yanbu. Figure 4 also shows a steady decline in concentrations as the air mass moves towards the southeast which might be attributable either to progressive dilution with cleaner air or alternatively to reduction in concentrations due to chemical reactions. Without further supporting information, it is not possible to clearly identify the causal factor. Such supporting information might include measurements of a passive (unreactive) tracer compound from which to assess the extent of dilution during transport.

ACKNOWLEDGEMENTS

Authors are indebted for financial support by Saudi Ministry of Higher Education and Deanship of Scientific Research (DSR) at King Abdulaziz University. This work was funded with a grant #2/H/1434.

REFERENCES

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.

Abdallah, M.-E., Atia, N., 2014. Atmospheric concentrations, gaseous–particulate distribution, and carcinogenic potential of polycyclic aromatic hydrocarbons in Assiut, Egypt. *Environmental Science Pollution Research* 1-11, doi 10.1007/s11356-014-2746-6.

Alghamdi, M.A., Alam, M.S., Yin, J., Stark, C., Jang, E., Harrison, R.M., Shamy, M., Khoder, M.I., Shabbaj, I.I., 2015a. Receptor modelling study of polycyclic aromatic hydrocarbons in Jeddah, Saudi Arabia. *Science of the Total Environment* 506-507, 401-408.

Alghamdi, M.A., Alam, M.S., Stark, C., Mohammed, N., Harrison, R.M., Shamy, M., Khoder, M.I., Shabbaj, I., Göen, T., 2015b. Urinary metabolites of polycyclic aromatic hydrocarbons in Saudi Arabian schoolchildren in relation to sources of exposure. *Environmental Research* 140, 495-501.

Akyuz, M., Cabuk, H., 2010. Gas-particle partitioning and seasonal variation of polycyclic aromatic hydrocarbons in the atmosphere of Zonguldak, Turkey. *Science of the Total Environment* 408, 5550-5558.

Bae, S., Pan, X.-C., Kim, S.-Y., Park, K., Kim, Y.-H., Kim, H., Hong, Y.-C., 2010. Exposures to particulate matter and polycyclic aromatic hydrocarbons and oxidative stress in schoolchildren. *Environmental Health Perspective* 118, 570-583.

Baek, S.O., Field, R.A., Goldstone, M.E., Kirk, P.W., Lester, J.N., Perry, R., 1991. A review of atmospheric polycyclic aromatic hydrocarbons: Sources, fate and behavior. *Water, Air and Soil Pollution* 60, 279-300

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.

Delgado-Saborit, J.M., Stark, C., Harrison, R.M., 2011. Carcinogenic potential, levels and sources of polycyclic aromatic hydrocarbon mixtures in indoor and outdoor environments and their implications for air quality standards. *Environment International* 37 383-392.

Delgado-Saborit, J.M., Aquilina, N., Baker, S., Harrad, S., Meddings, C., Harrison, R.M., 2010. Determination of atmospheric particulate-phase polycyclic aromatic hydrocarbons from low volume air samples. *Analytical Methods* 2, 231-242.

Dominguez-Morueco, N., Augusto, S., Trabalon, L., Pocurull, E., Borrull, F., Schuhmacher, N., Domingo, J.L., Nadal, M., 2015. Monitoring PAHs in the petrochemical area of Tarragona County, Spain: comparing passive air samplers with lichen transplants. *Environmental Science Pollution Research* doi 10.1007/s11356-015-5612-2.

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 Pollutution Research* 21, 558-567.

Galarneau, E., 2008. Source specificity and atmospheric processing of airborne PAHs: Implications for source apportionment. *Atmospheric Environment* 42, 8139-8149.

Gao, B., Wang, X.-M., Zhao, X.-Y., Ding, X., Fu, X.-X., Zhang, Y.L., He, Q.-F., Zhang, Z., Liu, T.-Y., Huang, Z.-Z., Chen, L.-G., Peng, Y., Guo, H., 2015. Source apportionment of atmospheric PAHs and their toxicity using PMF: Impact of gas/particle partitioning. *Atmospheric Environment* 103, 114-120.

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. *EnvironmentalToxicological Chemistry* 25, 1496-1502.

Habeebullah, T.M., 2013. Risk assessment of poly cyclic aromatic hydrocarbons in the Holy City of Makkah, Saudi Arabia. *International Journal of Environmental Science 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.

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 & Assessessment* 184, 3593-3612.

IARC, 2010. IARC Monographys on the Evaluation of Carcinogenic Risks to Humans. Volume 92, Some Non-Hetrocyclic Polycyclic Aromatic Hydrocarbons and Some Related Exposures, World Health Organization International Agency for Research on Cancer, Lyon, France.

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.

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, K., Jahan, S.A., Kabir, E., Brown, R.J.C., 2013. A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects. *Environment International* 60, 71-80.

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., Callen, M.S., 2000. A review on polycyclic aromatic hydrocarbon (PAH) emissions from energy generation. *Environmental Science & Technology* 34, 3051-3057.

Pies C., Joffmann, B., Petrowsky, J., Yang, Y., Ternes, T.A., Hofmann, T., 2008. Characterization and source indentification of polycyclic aromatic hydorcarbons (PAHs) in revier bank soils. *Chemosphere* 72, 1594-1601.

Ravindra, K., Sokhi, R., Van Grieken, R., 2008. Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. *Atmospheric Environment* 42, 2895-2921.

Sun, F., Lifflejohn, D. and Gibson, M.D., 1998. Ultrasonication extraction and solid phase extraction clean-up for determination of US EPA 16 priority pollutant polycyclic aromatic hydrocarbons in soils by reversed-phase liquid chromatography with ultraviolet absorption detection. *Analytica Chimica Acta* 364, 1-11.

Tobiszewski, M., Namiesnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. *Environmental Pollution* 162, 110-119.

Trasande, L., Urbina, E.M., Khoder, M., Alghamdi, M., Shabaj, I., Alam, M.S., Harrison, R.M., Sham, M., 2015. Polycyclic aromatic hydrocarbons, brachial artery distensibility and blood pressure among children residing near an oil refinery. *Environmental Research* 136, 133-140.

Wang, F., Lin, T., Feng, J., Fu, H., Guo, Z., 2015. Source apportionment of polycyclic aromatic hydrocarbons in PM2.5 using positive matrix factorization modeling in Shangai, China. *Environmental Science Proccesses Impacts* 17, 197-205

WHO, 2000. Air Quality Guidelines for Europe, Second Edition, World Health Organisation, Regional Office for Europe, Copenhagen, Denmark.

WHO, 2010. WHO Guidelines for Indoor Air Quality: Selected Pollutants, World Health Organization, Regional Office for Europe, Copenhagen, Denmark.

Xie, M., Barsanti, K.C., Hannigan, M.P., Dutton, S.J., Vedal, S. 2013. Positive matrix factorization of PM2.5 – eliminating the effects of gas/particle partitioning of semivolatile organic compounds. *Atmospheric Chemistry & Physics* 13, 7381-7393.

Yamasaki, H., Kuwata, K., Miyamoto, H., 1982. Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons. *Environmental Science & Technology* 16, 189-194.

Yunker M.B., Macdonald, R.W., Vingarzan, R., Michell, H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry* 33, 489-515.

Zhao, B., Zhang, S., Zhou, Y., He, D., Li, Y., Ren, M., Xu, Z., Fang, J., 2105. Characterization and quantification of PAH atmospheric pollution from a large petrochemical complex in Guangzhou: GC-MS/MS analysis. Microchemistry Journal 119, 140-144.

TABLE LEGENDS

Table 1: Total concentrations of PAH congeners at all sites (ng m^{-3})

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

FIGURE LEGENDS

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

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

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

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

Table 1: Total concentrations of PAH congeners at all sites (ng m^{-3}).

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	**$COD_{A\&B}$**	**$COD_{A\&C1}$**	**$COD_{B\&C1}$**
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	**$COD_{C2\&D}$**	**$COD_{C2\&E}$**	**$COD_{D\&E}$**
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

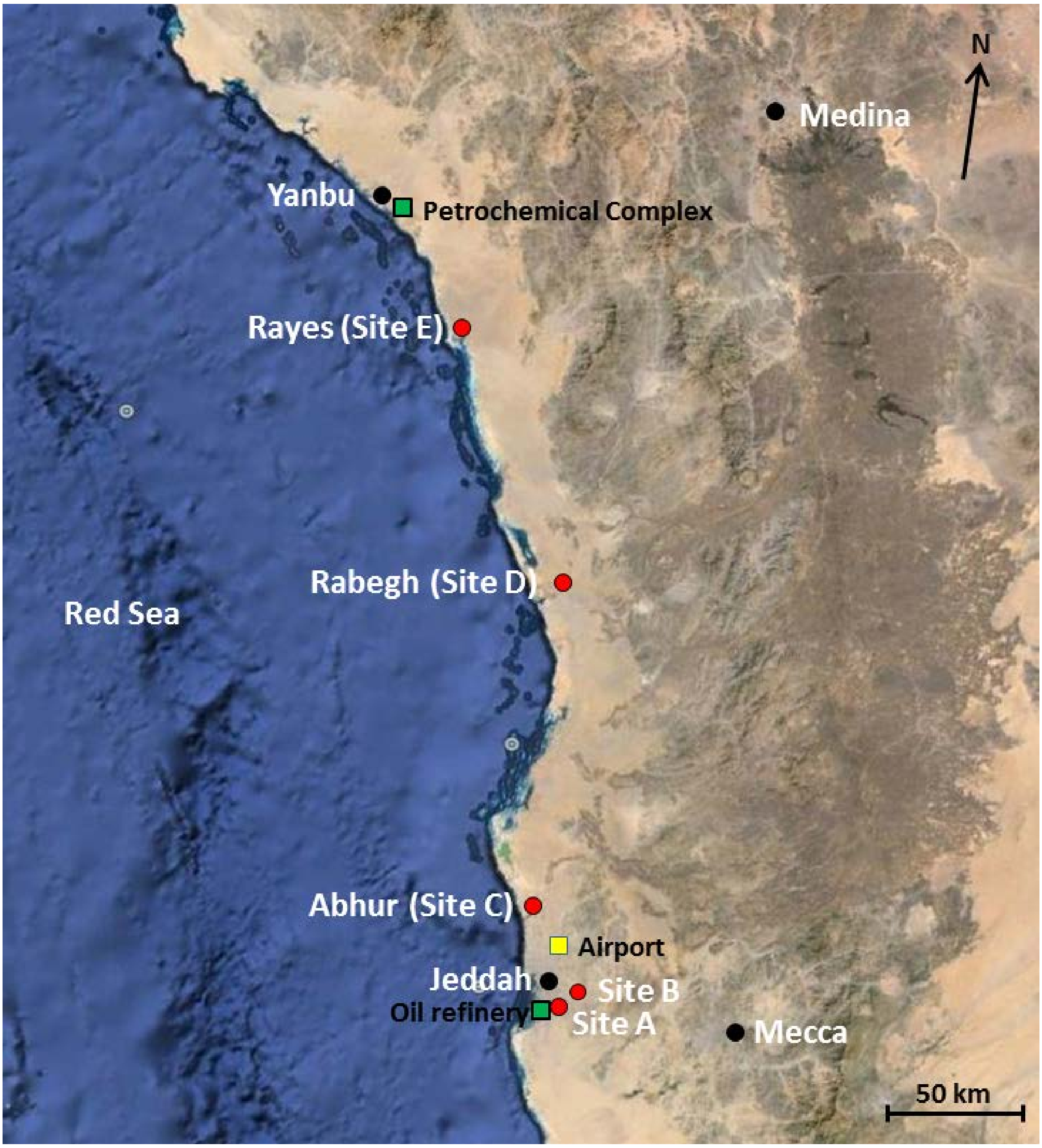

Figure 1: Locations of sampling sites and the city of Jeddah. The sites are: A-refinery; B-ring road; C-Abhur; D-Rabegh and E-Rayes.

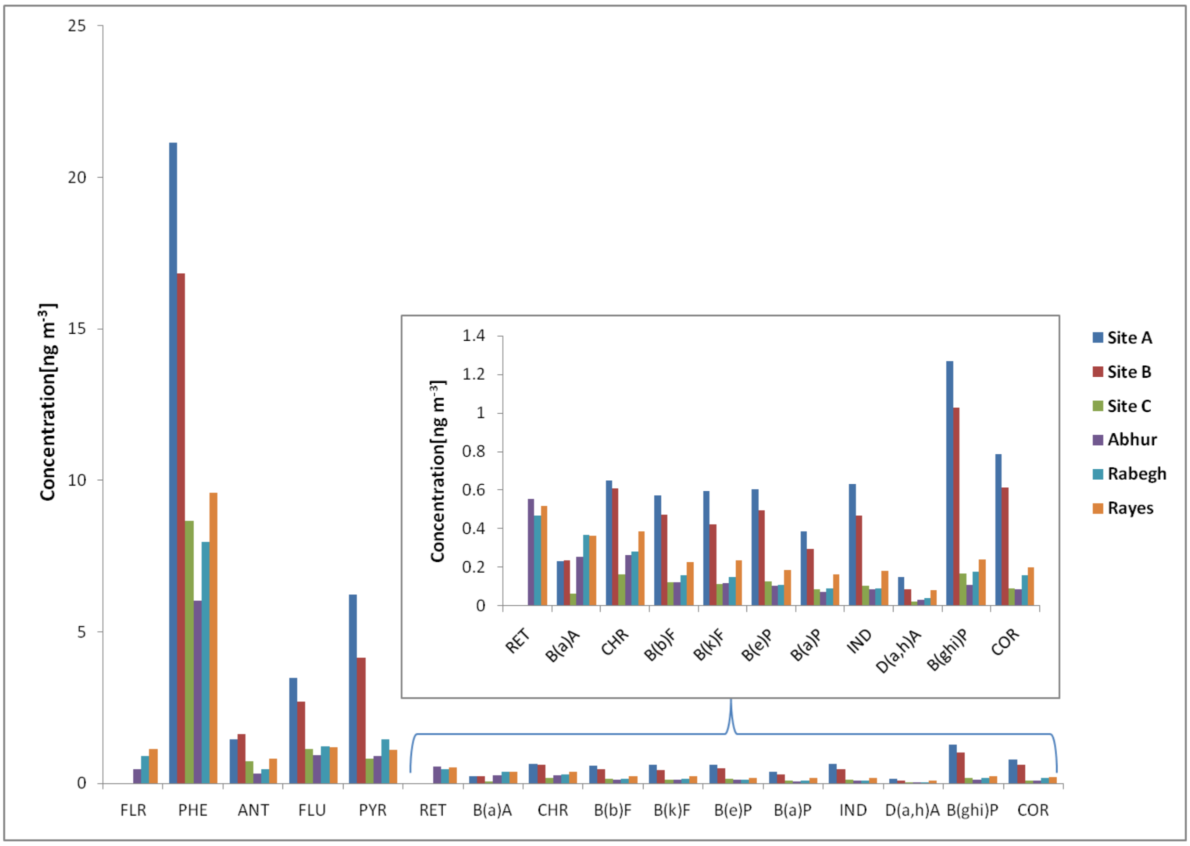

Figure 2: Average congener profile of PAH from both sampling campaigns at the five sites, including both campaign data for Site C. The site C data refer to the first campaign (1) and the Abhur data refer to the second campaign (2).

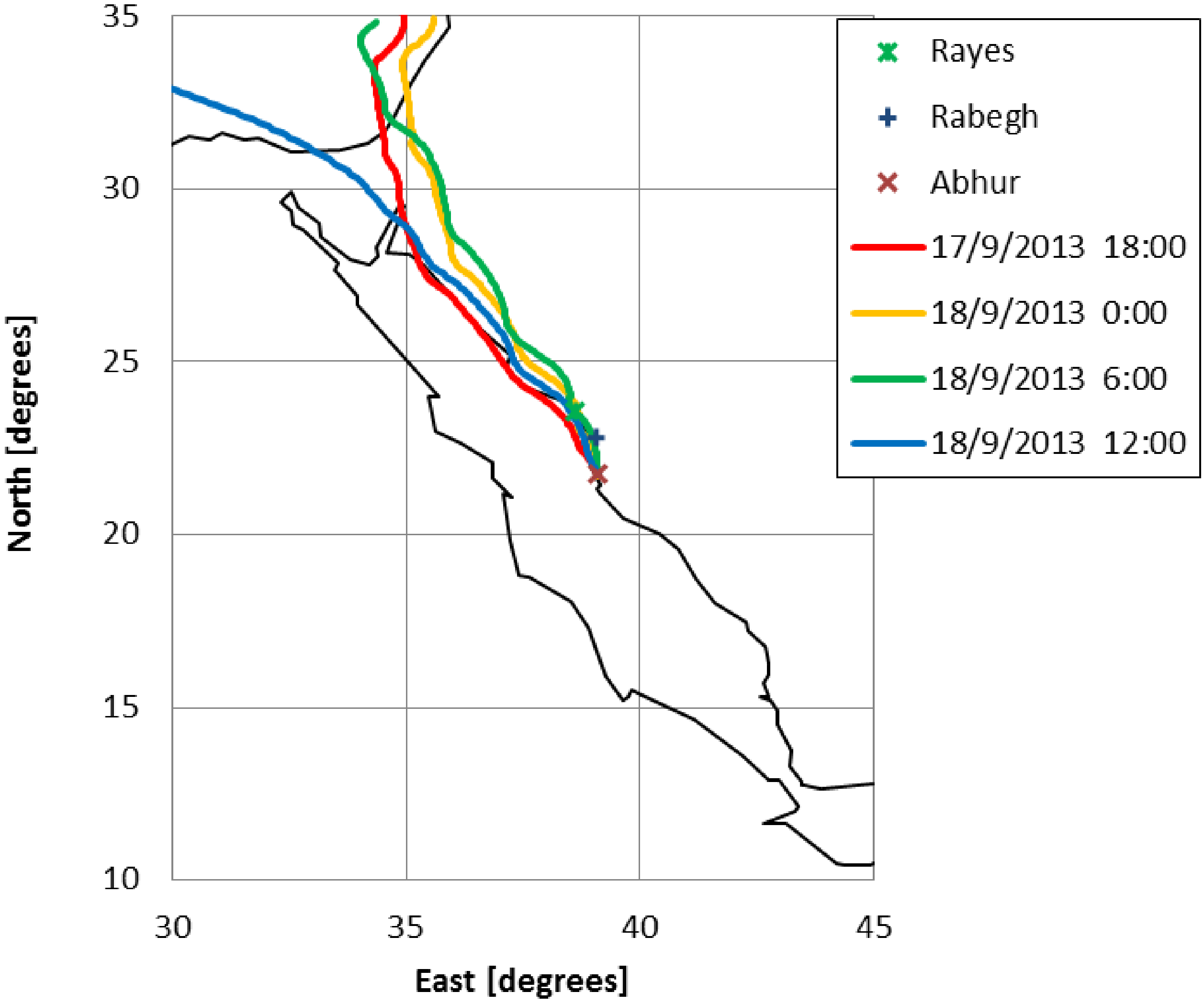

Figure 3: Air mass back trajectories to the the three sites for 17 September 2013 ending at 950 mb showing the air mass running parallel to the Red Sea coast.

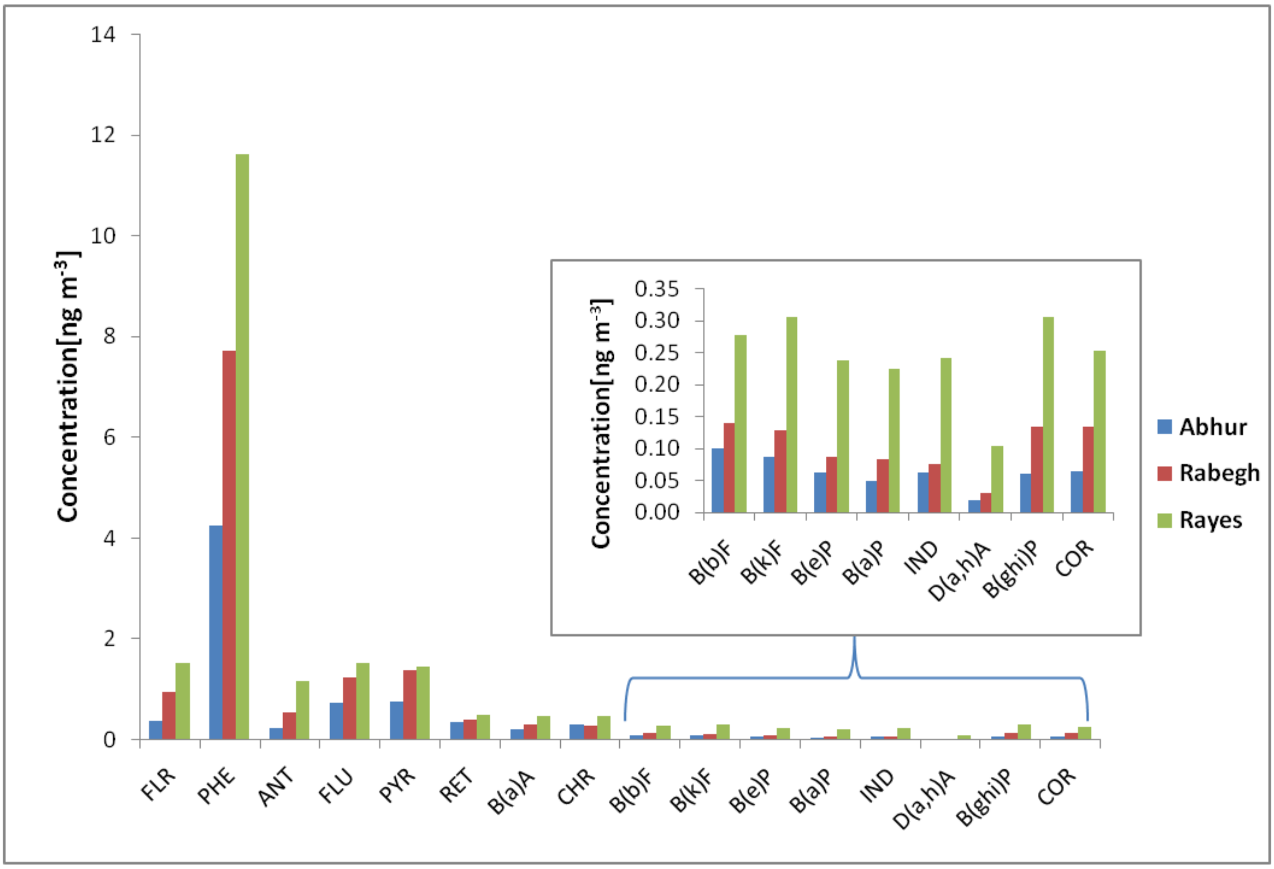

Figure 4: Average congener profile of PAH from the second sampling campaign including only air samples when the air mass travelled from north-west to south-east parallel to the Red Sea coast.