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Environmental Assessment of Polycyclic Aromatic Hydrocarbon Concentrations in Atmospheric Air at Daura Refinery

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) were measured in aerosol from air samples, which collected for the period from April 2012 to February 2013, in Baghdad city, at Daura Refinery. Aerosol samples were collected on cellulose fiber filters for 1.5 h in each site for the morning and evening time. These aerosol samples undergone soxhlet extraction.

After the extraction, 49 samples were analyzed by GC-MS in order to determin 16 PAH compounds. The parameters temperature, relative humidity and wind speed were measured during the measurement period. The PAH concentrations were different for location inside and outside Daura refinery. Naphthalene was the most abundant PAH detected in all points at the site sampling for all seasons. There is strong correlation between total suspended particles (TSP) and total polycyclic aromatic hydrocarbons (TPAH) (0.897, 0.966, 0.800) for spring, summer and autumn respectively. There was positive correlation between the total PAH concentrations and the relative humidity in the spring, autumn and winter seasons.

Keywords: Polycyclic Aromatic Hydrocarbon, Environmental, Daura Refinery.

التقييم البيئي لتركيز الهيدروكربونات العطرية متعددة الحلقات في الهواء الجوي لمصفى الدورة

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الخلاصة:

قيست تراكيز الهيدروكربونات العطرية متعددة الحلقات في عينات الهواء التي جمعت في الفترة من ابريل عام 2012 إلى فبراير عام 2013 ، في مصفى الدورة لمدينة بغداد. جمعت عينات الهواء على مرشحات ألياف السليلوز لمدة ساعة ونصف للموقع ولفترتي الصباح والمساء ثم استخلصت باستخدام جهاز السوكسليت. حلل 49 نموذج مستخلص بوساطة كروماتوغرافيا الغاز – مطيافية الكتلة (GC– MS) لتحديد 16مركب حلقي عطري (PAH) ، وقيست معلمات الأرصاد الجوية مثل درجة الحرارة والرطوبة النسبية وسرعة الرياح خلال فترة القياس. تفاوتت تراكيز هذه المركبات PAH بين الموقع الداخلي والخارجي لمصفى الدورة. لوحظ تركيز النفالثين الاكثر وفرة في جميع المواقع ولجميع الفصول . وجدت علاقة قوية بين تركيز الدقائق العالقة (TSP) و التركيز الكلي لمركبات العطرية الحلقية (TPAH) (0.897، 0.966، 0.800) لفصول الربيع والصيف والخريف على التوالي، و علاقة ايجابية بين التركيز الكلي للهيدروكربونات العطرية متعددة الحلقات والرطوبة النسبية في فصول الربيع، والخريف والشتاء

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1-Introduction

Polycyclic aromatic hydrocarbons (PAH) are composed of carbon and hydrogen atoms arranged in the form of fused benzene rings (linear, cluster or angular arrangement). There are hundreds of PAH compounds in the environment but in practice PAH, analysis is restricted to the determination of 16 compounds. Individual PAHs differ substantially in their physical and chemical properties [1, 2].

Polycyclic aromatic hydrocarbons (PAHs) belong to the group of persistent organic pollutants (POPs). These are organic contaminants that are resistant to degradation, they can remain in the environment for long periods, having the potential to cause adverse environmental effects. Some of them are susceptible to dispersion on a global scale because, in addition to having environmental persistence, they are semi-volatile under environmental conditions they move between the atmosphere and the Earth's surface in repeated, temperature-driven cycles of deposition and volatilization. POPs are truly multimedia contaminants which occur in all parts of the environment atmosphere, inland and sea waters, sediments, soils and vegetation. [3-5].

The general characteristics of PAHs are high melting and boiling points (therefore they are solid), low vapor, pressure and very low aqueous solubility, both of which tend to decrease with increasing molecular weight. PAHs are highly lipophilic and very soluble in various organic solvents. Aqueous solubility decreases for each additional ring [6-8].

In ambient air، PAHs are generally present in both the gaseous phase and in association with particular matter (PM). They are partitioned in varying proportions in the two phases depending on a number of factors including the vapor pressure of the PAH, the ambient temperature, humidity, precipitation, the amount and nature of the PM present in the atmosphere [9]. In general, at ambient air temperatures, two- and three-ringed PAHs are mostly found in the gaseous phase, whereas PAHs with five or more rings are primarily particle-associated and four-ringed PAHs are distributed between the two phases. The major source of PAHs is the incomplete combustion of organic material such as coal, oil, and wood.

There are few commercial uses for many PAHs. They are mostly used as intermediaries in pharmaceuticals, agricultural products, photographic products, thermosetting plastics, lubricating materials, and other chemical industries. Other PAHs may be contained in asphalt used for the construction of roads, as well as roofing tar. Precise PAHs, specific refined products, are used also in the field of electronics, functional plastics and liquid crystals [10, 11].

Polycyclic aromatic hydrocarbons affect organisms through various toxic actions. They have been shown to cause carcinogenic and mutagenic effects and also have been found to be potent immunosuppressants (decreasing immune function) [12-15].

Hundreds of polycyclic aromatic hydrocarbon (PAH) species have been separated and identified. Many analytical techniques have been developed and subsequently applied for the monitoring of these compounds in the environment. As highly efficient separation tools, Gc-Ms and HPLC have been used for analysing all kinds of samples containing complex components [16, 17].

This work presents the results obtained from the determination of the 16 PAHs from samples of the atmospheric air in two sites at Daura refinery. Aerosol samples were collected and analyzed by GC-MS device. The calibration curve was used to measure concentrations of PAHs compounds in atmospheric air samples.

2-Experimental

2.1 Sampling site characteristics

The sites were chosen near the pollution source and around it to measure the PAHs. Daura Refinery was operated in 1955, and it located at the southern region of Baghdad city on the right bank of the Tigris river. The collection of aerosol sampling occurred at two points for the location, inside site near the emission of PAHs and outside site near the urban area surrounding the site. Selection of these sites was based on local activities with varying traffic density and industrial activities.

2.2 Chemical and Standard material

Methanol (Fluka,99.8%) and dichloromethane (Fluka,99.8%) were used for extraction of PAH from TSP.

The standard individual material poly aromatic hydrocarbons (PAH) were Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene ,Fluoranthene, Pyrene, Benz(a)anthracene,Chrysene, Benzo(b)-fluoranthene,Benzo(k)fluoranthene, Benzo(a)pyrene, Dibenz-(a,h)anthracene, Benzo(ghi)perylene and Indeno(1,2,3-cd)pyrene from (company "Dr. Ehrenstorfer", Germany), purity (99.9%), solid. The solution concentration of standard individual compounds PAHs was ranged (5-350) µg/l. Solutions of these compounds (mixtures or single component) are soluble in acetonitrile or methanol.

2.3. Standard solution

The retention time of the individual compounds (PAHs) were measured with range concentration (5-350) µg/l. For the measurements, a 4-points calibration range are used for all PAH. The concentrations of compounds in the calibration curve were used as follow: (3.33, 36.47, 67.41, 334.22) µg/L.

The target compounds PAHs were identified by comparing with retention time of standard compound and with the mass spectra to estimated molecular weight at the Technology University Darmstadt (TUD) in Germany. The final concentration of compounds PAHs were calculated from calibration curve and converted to ng/m^3 [18].

2.4. Sampling and sample preparation

Cellulose filters (4.5 cm diameter, 47mm thickness from Schleicher & Schuell, Germany) were used to collect aerosol samples from environments. These filters were pre-heated at 70 ◦C for 45 min prior to use to reduce their water content. Before and after sampling the cellulose filter were weighted on an electronic balance to determine the total suspended particles (TSP) and stored at low temperature in proper container until further extraction and analysis [19].

49 Samples were collected from April 2012 to February of 2013 in Daura refinery using a low volume air sampler as called sniffer (RADECO, Inc., England) at a flow rate of 9 f^3 min^{-1}, leading to an average sample volume of 7.5 m^3. Flow rates were measured at the beginning and at the end of each sampling event. Sampling was done inside and outside of site twice a month for a period of 1.5 hours in the morning and evening using sniffer device. The samples were collected applying (2.0 - 4.0) m above ground. The ambient temperature and relative humidity (VAISALA model HM1, Finland), as well as wind rate were measured during the period.

2.5. Soxhlet extraction

49 samples were extracted for determining polycyclic aromatic hydrocarbon concentrations in air samples which were collected from sampling sites. Air samples were extracted by soxhlet device [20] using mixture of methanol and dichloromethane (1:1). The soxhlet extractor consisted of a 250 ml round-bottom flask, 50 ml extractor and water cooled condenser with water bath an arrangement enabling extraction of only one filter sample at time [21].

After extraction, the filter was removed and rinsed with a mixture of methanol and dichloromethane. The filtrate was concentrated to dryness by rotary evaporator (Yamato RE 510) at 60^{o}C under gentle vacuum. Then dissolve the dried sample in 5 ml methanol and filtered the solution with micro filter (0.22 µm, Minisart, Sartorius Stedim Biotech GmbH 37070 Goettingen, Germany) put in glass container and kept in low temperature.

2.6. GC/ MS analysis

All 16 PAHs were identified and quantified by using a Trace GC/MS spectrometer with MSD, ChemStation software (Agilent Technologies 5975C Series GC/ MSD, USA). Auto-sampler with Triple –Axis Detector. Gas chromatography (GC) equipped with a flame ionization detector (FID). The gas chromatographic column used was Zebron Guardian, phase:ZB-5MS, a non-polar, packed wih 5% phenyl methylsilox. Capillary column (L 30m × I.D. 0.25mm × df= 0.25µm). High-purity helium (99.99%) was used as carrier gas at a flow rate of 1.0 ml min^{-1}. The temperatures of the MSD ion source and quadrupole analyzer were kept at 230°C and 150 °C, respectively. The detection limit was 1 nanogram/liter The injected volume was 10 µl in splitless mode [22].

The GC oven temperature program was from 75 °C (hold for 3 min) to 235 °C (20 °C/min), then ramped to 300 °C (5 °C/min) and final temperature was 320 ^{o}C (10 ^{o}C/min, hold for 9 min). The analysis time per sample was 43min.

3. Results and discussion

3.1.TPAH (ΣPAH) and TSP concentrations in the site.

Forty nine samples were collected and quantified for 16 PAH compounds. The total suspended particulate (TSP) and total polycyclic aromatic hydrocarbons (TPAH) concentration in each season are listed along with temperature and relative humidity in Table 1. The high TSP concentrations in the spring season with range (967.26 – 3223.24) µg/m^3, while the high TPAH concentration in the summer season with range (242.77-952.84) ng/m^3, refer to a large variability during the sampling period probably attributed to meteorological variations during the sampling period. The temperature range was (15.79-46.42) °C and humidity range was (16.88 -59.99) in winter and summer season respectively.

Table 1- TSP and TPAH Concentrations during the sampling measurement period.

season	Location	Time	Temp °C	Hum.%	Wind rate m/s	Tsp µg/m^3	TPAHs ng/m^3
spring	Inside	Morn.	40.67	17.12	1.70	1177.98	40.80
		Even.	40.04	19.11	2.80	967.26	79.80
	outside	Morn	39.30	19.14	1.50	1650.04	73.20
		Even.	42.19	19.73	2.30	3223.24	149.70
Summer	Inside	Morn.	42.61	18.01	1.47	422.45	354.46
		Even.	46.35	33.72	1.17	331.50	242.77
	outside	Morn	39.86	20.40	1.03	962.30	952.87
		Even.	46.42	16.88	1.00	640.34	428.73
Autumn	Inside	Morn.	30.04	30.70	1.45	609.86	25.62
		Even.	33.08	26.30	1.50	476.69	27.60
	outside	Morn	25.94	36.79	0.60	1068.41	49.92
		Even.	35.23	22.25	1.00	810.88	55.86
Winter	Inside	Morn.	18.52	49.70	1.70	360.20	10.76
		Even.	20.10	43.43	3.20	280.23	11.03
	outside	Morn	15.79	59.99	1.00	626.53	9.15
		Even.	22.40	37.52	1.40	807.25	8.95

The influence of meteorological parameters such as temperature, relative humidity and wind speed on the PAH emissions was analyzed by statistical package for social scientist (SPSS) programm. The positive correlation between the total PAH concentration and the relative humidity was observed in the season's winter, spring and autumn respectively as listed in the table 2. Thus could be due to a depositional effect on the particulate matter of PAHs in the gas phase as a consequence of environmental humidity.

The positive correlation between the temperature and the total PAH concentration could be observed in both winter and summer while negative correlation in the spring and autumn seasons, indicated to existence extrusive relationship between temperature and TPAH in the chosen sites. There are strong correlation between TSP and TPAH (0.897, 0.966, 0.800) respectively for spring, summer and autumn, due that the higher concentration of total suspended particulate leads to the adsorption more molecules of PAHs compounds [23-25]. For the rate wind studied, no statistical significance was obtained.

Table 2- Calculation of Pearson Correlations of parameters in the different seasons.

Pearson Correlations – Winter

parameters	Temp. (°C)	Hum. %	Wind (m/s)	Tsp (mg/m^3)	TPAHs (ng/m^3)
Tsp (mg/m^3)	0.222	-0.130	-0.743	1	
TPAHs (ng/m^3)	-0.957*	0.953*	-0.409	-0.261	1

Pearson Correlation – Spring

parameters	Temp. (°C)	Hum. %	Wind (m/s)	Tsp (mg/m^3)	TPAHs (ng/m^3)
Tsp (mg/m^3)	-0.351	0.589	0.020	1	
TPAHs (ng/m^3)	-0.261	0.822	0.420	0.897	1

Pearson Correlations –Summer

parameters	Temp. (^oC)	Hum .%	Wind (m/s)	Tsp (mg/m^3)	TPAHs (ng/m^3)
Tsp (mg/m^3)	-0.671	-0.491	-0.614	1	
TPAHs (ng/m^3)	-0.817	-0.379	-0.468	0.966*	1

Pearson Correlations – Autumn

parameters	Temp. (^oC)	Hum. %	Wind (m/s)	Tsp (mg/m^3)	TPAHs (ng/m^3)
Tsp (mg/m^3)	-0.573	0.534	-0.986*	1	
TPAHs (ng/m^3)	0.027	-0.072	-0.845	0.800	1

** correlation at 99% confidence level.
* correlation at 95% confidence level.

3.2.PAHs concentrations

49 air sample collected and analysis by GC-MS to determine 16 PAHs. The retention time (t_R) of individual standard PAHs compounds were measured. The quantification analysis was based on a linear-least-squares equation from plot the concentrations of PAH versus peaks area of standard compound. Peaks identification were based on comparison of retention times of target PAHs with retention times of standard solutions. The retention time, molecular weight and equation of a straight line from calibration curve were listed in table 3.

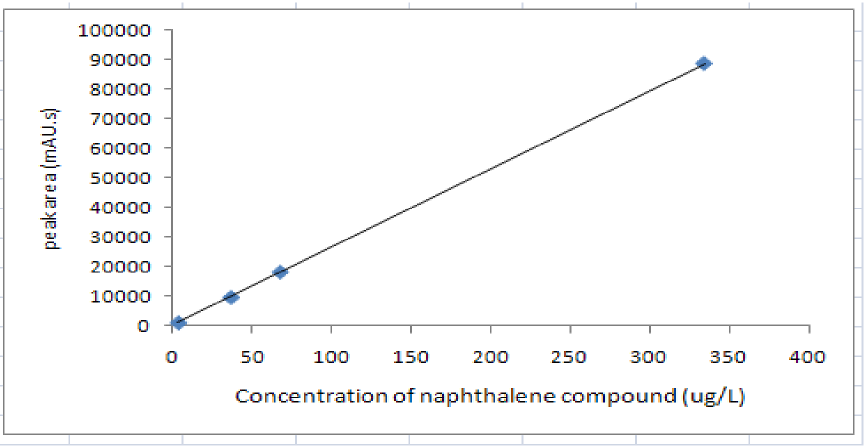
Figures 1 and 2 shows the calibration curve of Naphthalene, Fluorene, phenanthrene, pyrene and benzo[k]fluoranthene compounds.

Table 3- Summary of result for calibration curve to estimate concentration of PAHs compounds.

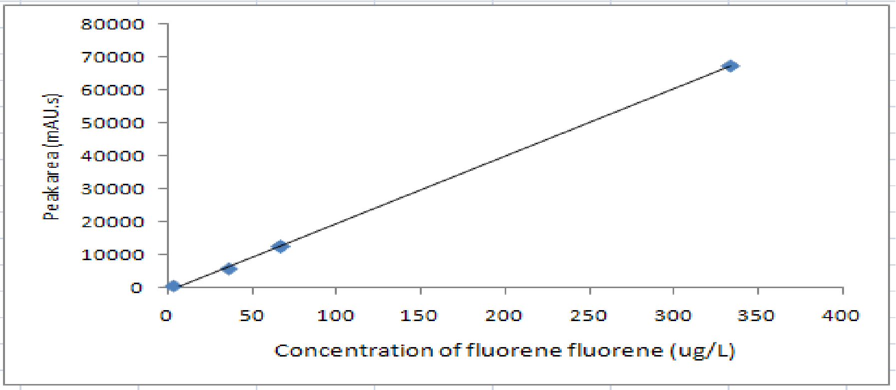
No.	PAHs	Abbreviation	M. wt g. mol^{-1}	t_R min.	equation of a straight line $\hat{y} = bc + a$
1	Naphthalene	Naph	128	8.386	264.3 c + 294.3
2	acenaphthylene	Acy	152	10.421	276.4 c - 198.8
3	acenaphthene	Ace	153	10.660	191.8 c - 149.3
4	Fluorene	Flu	166	11.301	203.7 c - 954.5
5	Phenanthrene	Phe	178	12.622	369.6 c - 3367
6	Anthracene	Ant	178	12.706	381.8 c - 4948
7	Fluoranthene	Flt	202	15.181	341.5 c - 1559
8	Pyrene	Pyr	202	15.900	350.5 c - 1400
9	Benzo(a) Anthracene	B[a]A	228	22.549	300.1 c - 3164
10	Chrysene	Chry	228	22.793	306.6 c - 1542
11	Benzo(b) Fluoranthene	B[b]F	252	32.452	291.7 c - 2297
12	Benzo(k) Fluoranthene	B[k]F	250	32.587	65.91 c - 274.1
13	Benzo(a) Pyrene	B[a]P	250	33.712	54.63 c - 39
14	Indeno(1,2,3-cd) Pyrene	Ind(cd)P	276	37.933	107.2 c + 96.22
15	Dibenzo(a,h) anthracene	dBA	278	38.125	147.0 c - 1039
16	Benzo(g,h,i) Perylene	BghiP	276	39.024	133.5 c - 534.7

C:[concentration] ug/l. $\hat{y}$: estimated from calibration curve.

From table 3 could be observed that retention time increased with increased molecular weight of compound.



A- Naphthalene



B- Fluorene

Figure 1- Calibration curve of standard compounds: A- naphthalene and B-fluorene.

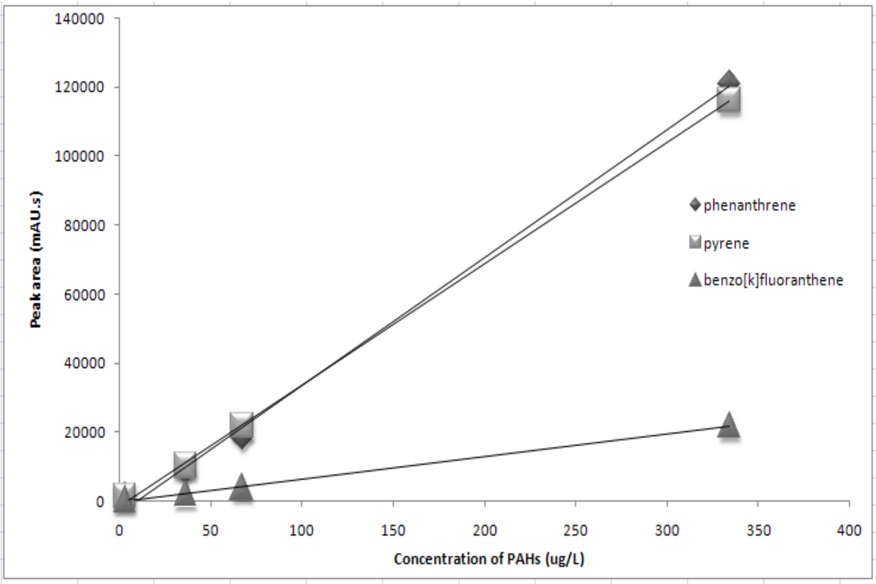


Figure 2- Calibration curves of standard compounds phenanthrene, pyrene and benzo[k]fluoranthene

The average concentrations of individual PAHs measured in ambient air at the various season are present in table (4a and 4b). Naphthalene was the most abundant PAH detected in the all points in the site sampling for all season. In the summer, naphthalene concentration ranged (479.8 -971) ng/m^3, while in the winter concentration ranged (19.3-24.7) ng/m^3. The second compound was anthracene concentration ranged (25.04-739) ng/m^3 in the summer, while in winter was acenaphthene with range (3.06 – 3.7) ng/m^3. Variation of individual compounds concentration shows in the figure-3.

Table 4a- Average concentrations of individual PAHs (ng/m^3) in Summer Season.

compounds	Inside/morning	Inside /evening	Outside/morning	Outside/evening
	Mean ± Confidence interval	Mean ± Confidence interval	Mean ± Confidence interval	Mean ± Confidence interval
Naph	971 ± 174.157	479.807 ± 70.824	875.33 ± 136.595	620.552 ± 106.001
Acy	1.233 ± 0.117	4.866 ± 0.310	1.966 ± 0.117	1.705 ± 0.204
Ace	2.8 ± 0.202	6.173 ± 2.574	8.9 ± 0.351	2.628 ± 0.145
Flu	6.866 ± 0.309	5.305 ± 0.220	7.9 ± 0.203	6.973 ± 0.529
Phe	60 ± 39.905	7.911 ± 0.169	43 ± 12.339	25.636 ± 3.435
Ant	739 ± 80.452	25.048 ±9.995	669 ± 87.084	28.809 ± 12.601
Flt	6.833 ± 0.585	1.925 ± 0.222	6.4 ± 1.073	4.103 ± 0.292
Pyr	27.666 ± 8.198	3.915 ± 0.159	16.666 ± 5.105	15.544 ± 8.109
B[a]A	1.9 ± 0.202	ND	3.933 ± 0.234	2.966 ± 0.117
Chry	ND	ND	0.733 ± 0.117	ND
B[b]F	ND	ND	2.966 ± 0.310	0.733 ± 0.117
B[k]F	ND	ND	ND	ND
B[a]P	ND	ND	4.933 ± 0.234	3.933 ± 0.117
Ind(cd)P	ND	ND	ND	1.5 ± 0.203
dBA	2.9 ± 0.202	ND	3.333 ± 0.117	1.333 ± 0.117
BghiP	ND	ND	ND	1.666 ± 0.117

Mean ($\bar{X}$) when n=3 (ng/m^3). confidence interval = $t \times \frac{\sigma_{n-1}}{\sqrt{3}}$, degree of freedom (df)=2 and t_{tab}=4.303 for n=3 (No. of measurements)…………..ND: not detected.

Table 4b- Average concentrations of individual PAHs (ng/m^3) in Winter Season

Compound	Inside/morning	Inside /evening	Outside/morning	Outside/evening
	Mean ± Confidence interval	Mean ± Confidence interval	Mean ± Confidence interval	Mean ± Confidence interval
Naph	24.729 ± 6.511	19.328 ± 3.134	19.656 ± 2.276	20.641 ± 3.8248
Acy	1.187 ± 0.217	ND	1.349 ± 0.371	0.838 ± 0.1205
Ace	3.707 ± 1.722	3.643 ± 1.335	3.2085 ± 0.046	3.061 ± 0.2062
Flu	0.466 ± 0.165	0.504 ± 0.170	0.459 ± 0.099	0.323 ± 0.2261
Phe	4.280 ± 1.781	4.318 ± 1.222	4.573 ± 0.402	2.757 ± 0.1292
Ant	0.572 ± 0.161	ND	0.530 ± 0.124	0.766 ± 0.0882
Flt	1.006 ± 0.014	3.816 ± 1.451	3.407 ± 1.250	1.557 ± 0.1764
Pyr	ND	3.056 ± 0.381	1.269 ± 0.093	1.902 ± 0.1888
B[a]A	ND	ND	ND	ND
Chry	0.6215 ± 0.056	ND	ND	ND
B[b]F	2.268 ± 0.180	1.661 ± 0.122	ND	ND
B[k]F	ND	ND	ND	ND
B[a]P	2.515 ± 0.224	ND	ND	ND
Ind(cd)P	2.259 ± 0.251	1.8515 ± 0.043	3.285 ± 0.132	1.383 ± 0.2062
dBA	ND	ND	ND	ND
BghiP	2.286 ± 0.389	2.775 ± 0.466	5.135 ± 0.436	1.1930.2311

Mean ($\bar{X}$) when n=3 (ng/m^3). confidence interval = $t \times \frac{\sigma_{n-1}}{\sqrt{3}}$, degree of freedom (df)=2 and t_{tab}=4.303 for n=3 (No. of measurements)………..ND: not detected.

Tables 4a and 4b illustrated the order of increasing concentrations of PAH related to seasons , it seem, that PAH concentration in summer is higher than winter, due to happen heavy rain before the measurement process, which led to clean air from pollutants (PAH).

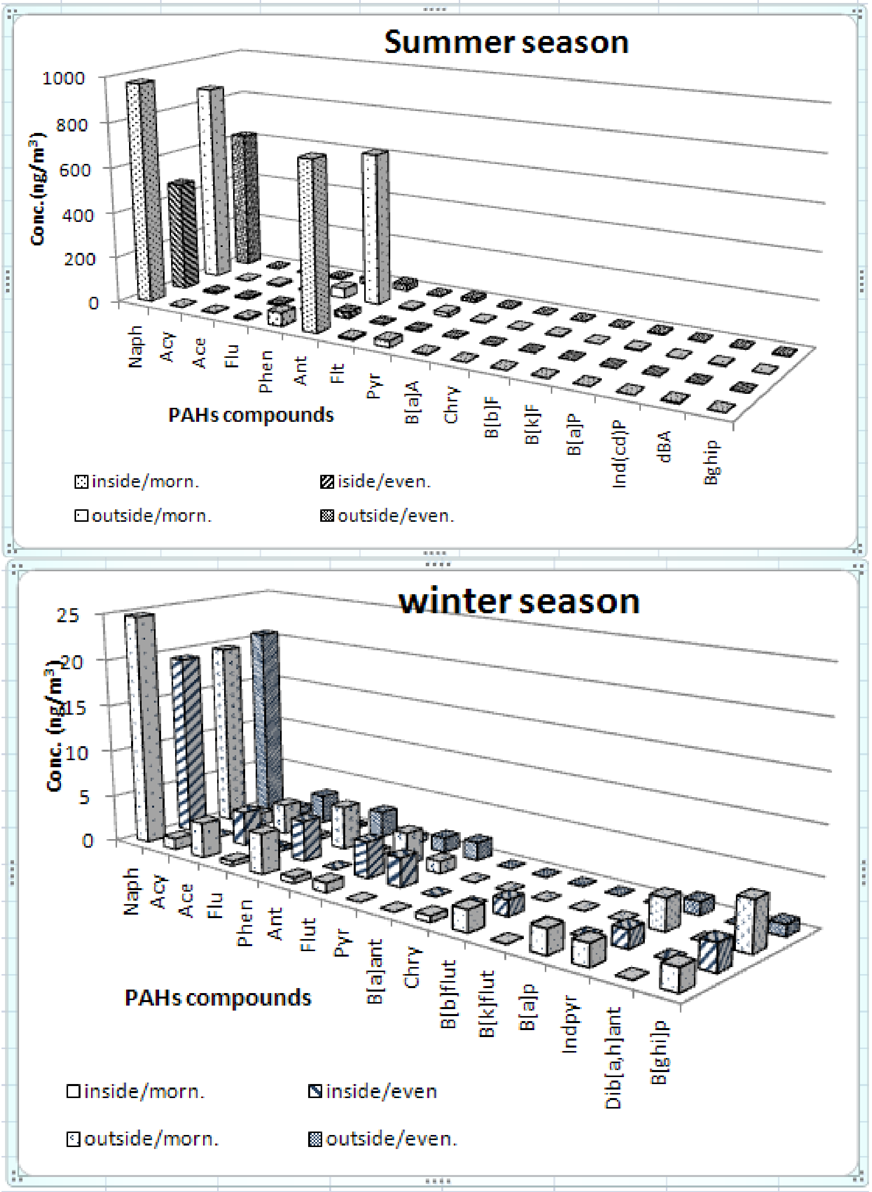


Figure 3- Individual compounds concentrations in the summer and winter seasons.

The results illustrate that most of the compounds emitted from the Daura Refinery are the low molecular weight ranged between (128-178) g / mol, due to several factors, including the quality of fuel used such as crude oil, which is the source of the emission of these compounds into the atmosphere. The most important factors that influence the distribution and the presence of these compounds in the air are the temperature, wind speed and wind direction. Figure 4 shows some charts of air samples were analysis by GC-MS to identify the compound in mixture from molecular weight..

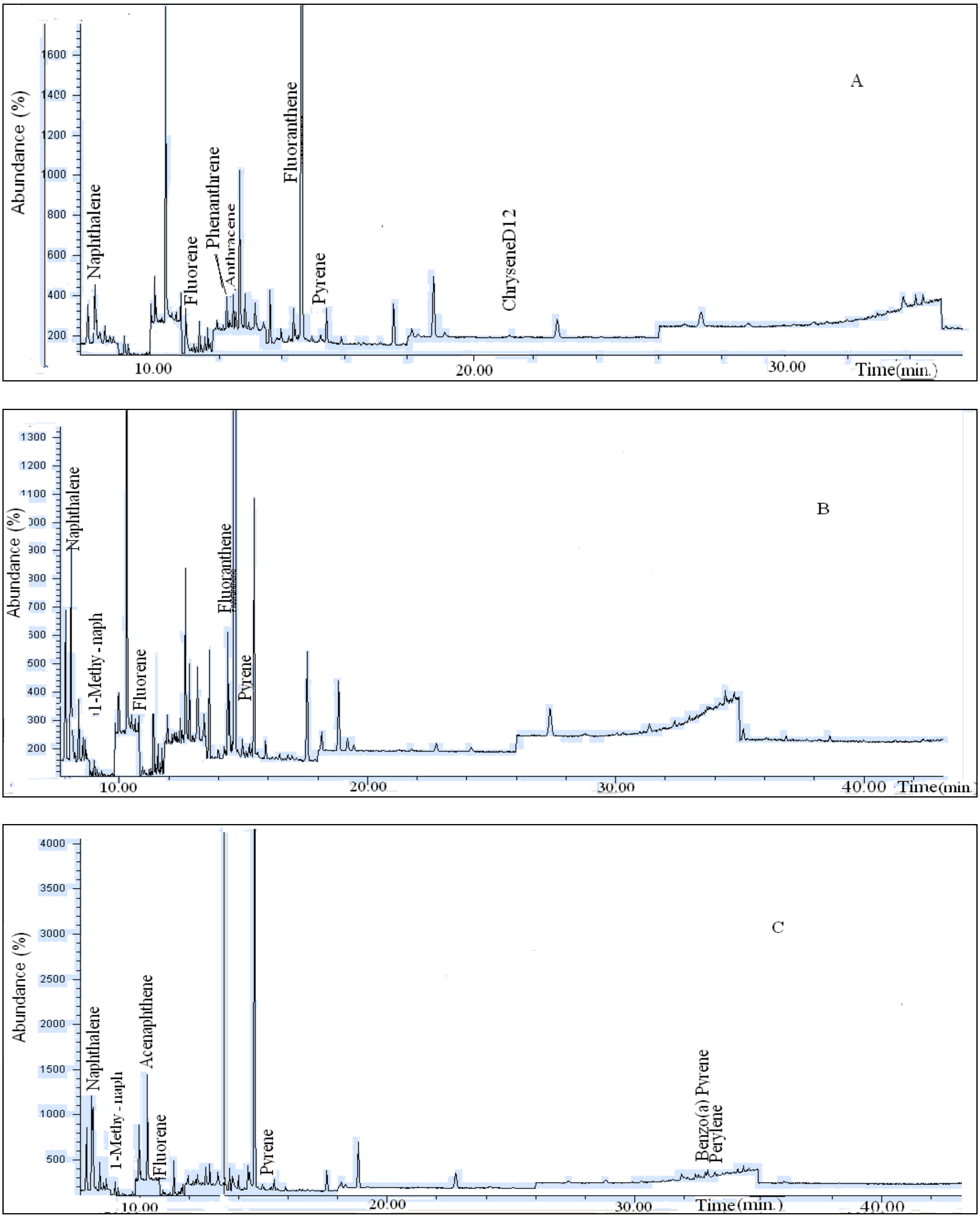


Figure 4- GC-MS charts of some air samples from Daura refinery: A-inside/morn., B-inside/even., C-outside/morn.

Conclusion

The concentrations of 16 PAHs, TPAH, and TSP in all seasons at two points in the Daura refinery were observed. Average concentrations of individual PAHs varied from 0.05 ng/m^3 to 971 ng/m^3. Positive correlation between TPAH and TSP with meteorological condition by the SPSS was found.

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References

1. Wild, S.R. and Jones, K.C. **1995**. Polynuclear aromatic hydrocarbons in the United Kingdom environment: a preliminary source inventory and budget. *Environment Poll*., 88, pp: 91-95.
2. Zoccolillo, L. Liberti, A. and Brocco, D. **1972**. Determination of polycyclic hydrocarbons in air by gas chromatography with high efficiency packed columns. *Atmospheric Environment*, 6, pp: 715-720.
3. Maliszewska-Kordybach, B. **1999**. Sources concentrations, fate and effects of polycyclic aromatic hydrocarbons (PAHs) in the environment. Part A: PAHs in Air. *Polish Journal of Environmental Studies*, 8(3), pp: 131-136.
4. Paterson, S. and Mackay, D. A .**1989**. Model illustrating the environmental fate exposure and human uptake of the persistent organic chemicals. *Ecol. Modeling*, 47, pp: 85-91.
5. Wania, F. and Mackay, D. **1996**. Tracking the distribution of persistent organic pollutants. *Environment Sci. Technology*, 30, pp: 390-396.
6. Rajput, N. and Lakhani, A. **2010**. Measurement of polycyclic aromatic hydrocarbon in an urban atmospheric of Agra, India. *Atomósfera*, 23(12), pp:165-183.
7. Weingartner, E. Burtscher, H. and Baltensperger, U. **1997**. Hygroscopic properties of carbon and diesel soot particles. *Atmos. Environ*., 31 (14), pp: 2311-2327.
8. Skupinska , K. Misiewicz, I. and Kasprzycka-Guttman, T. **2004**. Polycyclic aromatic hydrocarbons : physicochemical properties, environmental appearance and impact on living organisms. *Acta Poloniae Pharmaceutica – Drug Research*, 61(3), pp: 233-240.
9. Nirat, R. and Anita, L. **2009**. Measurements of polycyclic aromatic hydrocarbons at an industrial site in India. *Environ. Monitor Assess*, 50, pp: 273–284
10. Cerniglia, C. **1992.** Biodegradation of polycyclic aromatic hydrocarbons. *Biodegradation*, 3. pp: 351–368.
11. Freeman, D. J. and Cattell, F. R. **1990**. Wood burning as a source of atmospheric polycyclic aromatic hydrocarbons. *Environ Sci. Technology*, 24, pp: 1581–1585.
12. Lim, L. H., Harrison, R. M. and Harrad, S. **1999**. The contribution of traffic to atmospheric concentrations of polycyclic aromatic hydrocarbons. *Environ Sci. Technology*, 33, pp: 3538–3542.
13. Juhasz, A. and Naidu, R. **2000**. Bioremediation of high molecular weight polycyclic aromatic hydrocarbons: a review of the microbial degradation of benzo[a]pyrene. *Int. Bio-deteriorate Bio,* 45, pp: 57–88.
14. Allan, L. Schlezinger, J. and Shansab, M. **2006**. CYP1A1 in polycyclic aromatic hydrocarbon induced B lymphocyte growth suppression. *Biochemist Biophysics Res. Common*, 342(1), pp: 227-235.
15. Fekete, S. **2009**. Shell and Small Particles: Evaluation of New Technology. *J. of Pharmaceutical and Biomedical Analysis*, 49, pp: 64-71.
16. Gritti, F. and Guiochon, G. **2010**. Achieving Full Performance of Columns by Optimizing HPLC Instruments. *J. of Chromatograph*. A, 1217, pp: 3000-3012.
17. Joost, C. L. Wouter, O. Peter, H. V. and Piet, B. **1996**. Poly dimethyl -siloxane as an elastic material applied in a capacitive accelerometer. *J. Micromesh Microeng*. 6, pp: 52–54.
18. Rasdy, N. F. Sanagi, M. M. and Ahmedy, A. N. **2008**. Determination of polycyclic aromatic hydrocarbons in palm oil mill effluent by soxhlet extraction and gas chromatography-flame ionization detection. *Malaysian Journal of Analytical Sciences,* 12(1), pp: 33-39.
19. Ximei, H. Guoshun, Z. Yele, S. and Zhisheng, A. **2006**. Characteristics and sources of polycyclic aromatic hydrocarbons and fatty acids in PM2.5 aerosols in dust season in China. *Atmospheric Environment*, 40, pp: 3251–3262.
20. Husain, K. I. **2003**. Separation and determination of polycyclic aromatic hydrocarbons in Iraq environmental samples. Ph.D. Thesis. Department of Chemistry, College of Education- Ibn Al-Haitham, University of Baghdad. Baghdad, Iraq.

21. Christensen, A. Ostman, C. and Westerholm, R. **2005**. Ultrasound-assisted extraction and online LC–GC–MS for determination of polycyclic aromatic hydrocarbons (PAH) in urban dust and diesel particulate matter. *Anal. Bioanal. Chem*., 381. pp: 1206–1216.

22. Menezes, H.C. and Cardeal, Z. **2011**. Determination of polycyclic aromatic hydrocarbons from ambient air particulate matter using a cold fiber solid phase micro extraction gas chromatography–mass spectrometry method. *J. Chromatogr*., A, 1218, pp: 3300–3305.

23. Bergvall C. **2009**. Methods for determination of benzo(a)pyrene and high molecular weight (300 Da) polycyclic aromatic hydrocarbons in particulate matter from ambient air and vehicle exhausts. Ph. D. Thesis. Department of Analytical Chemistry, Stockholm University. Stockholm, Sweden.

24. Bjorseth, A. and Ramdahl, T. **1985**. *Handbook of Polycyclic Aromatic Hydrocarbons*. Third Edition. Dekker, New York.

25. Dias R. **1987**. *Handbook of Polycyclic Hydrocarbons*. Second Edition Elsevier, Amsterdam.