Pak. J. Biotechnol. VOL. 15 (2) 445-450 (2018) ISSN Print: 1812-1837
ww.pjbt.org ISSN online: 2312-7791

DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN SOIL AT AL-NAHRAWAN BRICKS FACTORY

Thamera K. M. Al-Rudaini[1] and Israa M.H. Almousawi[2]

[1]Ministry of Science and Technology, Baghdad, Iraq. [2] Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq. E. mail: [2]israa_mousawi@yahoo.com

Article received 8.4.2018, Revised 1.6.2018, Accepted 10.6.2018

ABSTRACT

The concentration of sixteen polycyclic aromatic hydrocarbons were determined in soil samples at AL-nahrawan bricks factory. The measured period was two seasons' summer and winter. The soil samples collected from surface and depth chosen site and analyzed by GC apparatus.

The most abundant compounds in the summer season were naphthalene, acenaphthene, fluorene, pyrene and benzo [a] anthracene, while in the winter were naphthalene, acenaphthene, fluorine, benzo [k] fluoranthene, benzo [a] pyrene. The concentrations of 16 PAH in the summer were higher than in the winter season.

Key word: AL-nahrawan bricks factory, PAHs, GC analysis.

1- INTRODUCTION

They are many pollutants in the environmental according to the developments in the many sides of the life especially in industry side, when used oil, black oil, coal and other fuels. Pollution includes air, water and soil. Soil pollution one of the dangerous pollution in the world because effect on the organisms. There are many pollutants in the environment one of them was polycyclic aromatic hydrocarbon. Polycyclic aromatic hydrocarbons (PAHs) are organic compounds consist of two or more fused benzene rings. PAHs as pure chemicals are white or yellowish crystalline compounds**.**

These compounds belong to group of the most dangerous pollutants occurring in environment due to anthropogenic activity. Their origin is connected with combustion of fossil fuels and organic matter, mining and ore processing as the group of the most important sources of PAHs (Khan and Ghouri 2011; Hawthorne and Kreitinger 2006, Robinson et al., 2008).

The United States Environmental Protection Agency (USEPA) has included sixteen PAHs in a list of priority pollutants as shown in figure 1.

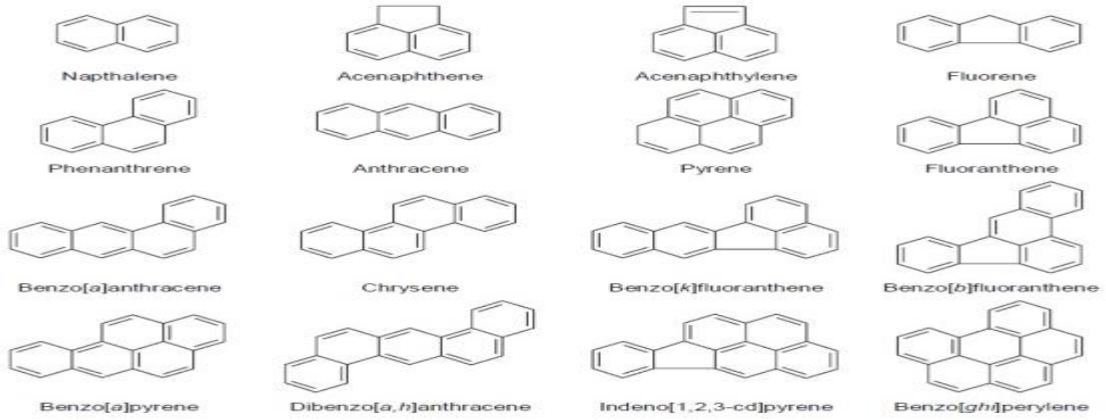

Figure 1: Structures of 16 PAHs.

This work includes collocation of soil samples from AL-nahrawan bricks factory at Baghdad city for two seasons. Sixteen polycyclic aromatic hydrocarbons concentrations were determined in surface and depth soil at the chosen site for summer and winter seasons. Soil samples were analyzed by GC apparatus.

2- MATERIALS AND METHODS

2.1 Chemicals and Standard Materials: Chemicals, solvents and apparatus which were used in

the experimental methods as shows in table 1 and 2.

Table 1: Chemical materials and solvents.

Substance	Specification	Origin	Activity
Acetone	Liquid C_3H_6O 99%	BDH, England	Solvent
Hexane	Liquid ,C_6H_{14}	BDH, England	Solvent
Methanol	Liquid ,CH_3OH	Riedl –De –Haen AG	Solvent
16 PAHs Standards	Solids	PAH Research Institute, Germany	Used in GC calibration curves

Table 2: Apparatus and accessories.

Instrument	Specification	Origin	Activity
Hand Shovel	-	Local	Remove soil from surface
Soxhlet	250 mL round-bottom flask, 50 mL extractor	Halalab	Extraction of PAHs from soil samples
Micro filter	Syringe filter pore size 0.2 µm	Hangzhou a now Co .LTD	Filtration for GC analysis
Gas Chromatography (FID detector)	Agilent	Germany	Estimation the PAHs in soil samples

2.4 Standard Solution: Retention times for standard individual sixteen of polycyclic aromatic hydrocarbons were measured in the GC apparatus. Stock solution was prepared by dissolving every PAH compound in methanol. These solutions were used for GC calibration curve with concentrations range (3-13) ppm.

2.5 GC analysis: The twelve soil samples were analyzed by GC apparatus to determine the concentration of sixteen PAHs compounds (Lau et al., 2010, Obint et al., 2013). Detector temperature was kept at 280 °C. The transfer line and ion source temperature was 90 ^{0}C (hold for 1 min) to 150 ^{0}C (10 ^{0}C/min) then ramped to 300 ^{0}C (5 ^{0}C/ min) and final temperature was 300 ^{0}C (5 ^{0}C/ min, hold for 12 min). The analysis time for every sample was 50 minutes.

2.2 Description of sampling sites: Sampling site selection is an important step in environmental pollution studies. Sampling sites were chosen near the source of emission of pollutants and around it to measure the PAHs. AL-nahrawan bricks factory were collection consists of about 300 production units. It located in south-east of Baghdad as shown in figure 2. The height of chimney is about 40 m and the used fuel is black oil.

2.3 Sampling and sample extraction: The surface soil samples were collected using hand shovel and measuring tape, as well as mechanical shovel in AL-nahrawan bricks factory site. The monitoring of PAHs was focused on the surface soil and a depth 30 cm of sediment surface for chosen site. Twelve soil samples were collected during summer and winter seasons from January to august 2017.

Figure (2): AL-nahrawan bricks factory

A 20 gm from soil sample was dried for four hours at 60 ^{o}C and grinded. Ground soil was put into the soxhlet apparatus using two solvent acetone and hexane (1:1) for about 15 hours. (Khan et al., 2005, Haleyuretal et al., 2016, Dong et al., 2012) After extraction, the extract was removed from the soxhlet apparatus and filtered

through filter paper. The solvents were removed to dryness using a rotary evaporator (Yamato RE 510) at 60 °C under gentle vacuum. The dried samples were dissolved in 5 ml methanol and filtered using micro filter. The solution was kept in glass container at low temperature before analysis.

3-RESULTS AND DISCUSSION

The retention time of standard individual policyclic aromatic hydrocarbons was measured according to the temperature programmer's (paragraph (2.5)) and calculated the linearity equation for every compound as shown in table 3.

Table 3: GC summary results of retention time and linearity equation.

No.	PAHs	Retention time min.	Equation of a straight line $\hat{Y} = ac + b$
1	Naphthalene	6.457	0.444 c -0.267
2	Acenaphthylene	10.377	0.276 c – 0.198
3	Acenaphthene	10.979	0.191 c -0.149
4	Fluorene	12.740	0.25 c -0.55
5	Anthracene	15.161	1.954 c - 2.018
6	Phenanthrene	16.449	2.236 c- 6.879
7	Fluoranthene	21.502	0.732 c + 0.289
8	Pyrene	22.422	1.236 c - 1.379
9	Benzo(a) Anthracene	27.878	5.554 c -11.331
10	Chrysene	32.545	0.306 c – 1.542
11	Benzo(b) Fluoranthene	32.463	3.344 c -4.029
12	Benzo(k) Fluoranthene	33.445	0.650 c 0.274
13	Benzo(a) Pyrene	33.665	0.757 c - 2.486
14	Indeno(1,2,3-cd) Pyrene	35.224	1.071 c + 0.096
15	Dibenzo(a,h) anthracene	36.894	0.147 c -1.039
16	Benzo(g,h,i) Perylene	37.684	0.133 c – 1.34

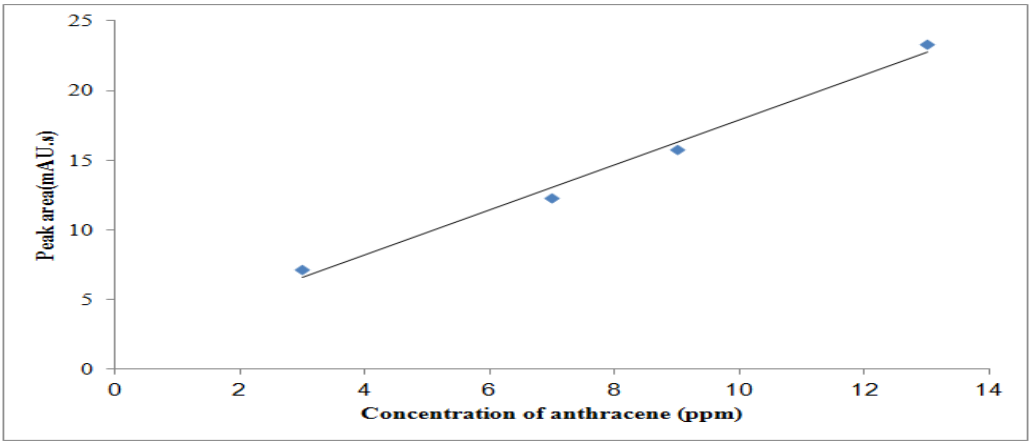

Figure 3: Calibration curve of standard anthracene compound.

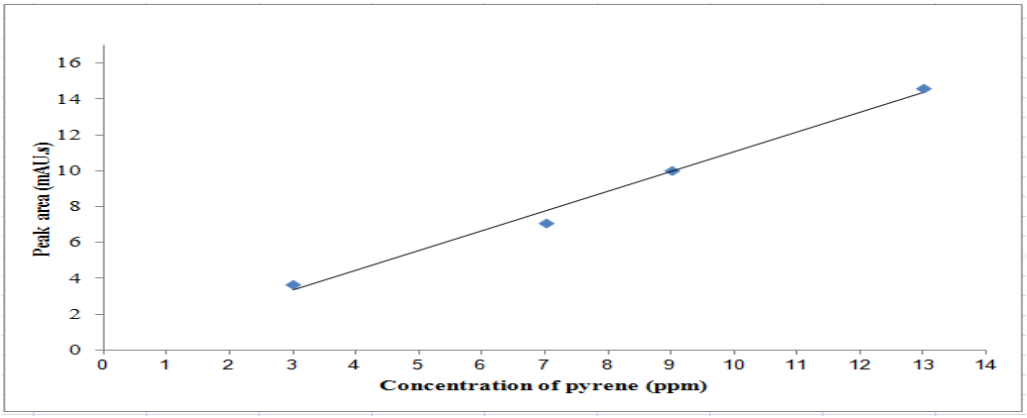

Figure 4: Calibration curve of standard pyrene compound.

The mean concentrations of polycyclic aromatic hydrocarbon compounds in soil samples were calculated by linearity equation after comparison with the retention time of standard compound for summer and winter seasons as shown in tables 4 and 5.

Table 4: Mean concentration of the individual PAH (µg/gm) measured in summer at AL-nahrawan bricks factory using GC analysis.

	Surface soil	Depth soil
Compound	Mean ± Confidence interval*	Mean ± Confidence interval
Naphthalene	195.078 ± 0.195	2.038 ±0.094
Acenaphthylene	ND	ND
Acenaphthene	14.371 ± 0.615	5.081 ± 0.076
Fluorene	15.475 ± 0.089	6.793 ± 0.204
Phenanthrene	2.315 ± 0.195	1.424 ± 0.256
Anthracene	1.958 ± 0.129	1.141 ± 0.046
Fluoranthene	ND	ND
Pyrene	10.84 ± 0.179	15.452 ± 0.153
Benzo[a]anthracene	3.255 ± 0.359	4.012 ± 0.002
Chrysene	ND	ND
Benzo[b]fluoranthene	1.713 ± 0.219	1.424 ± 0.061
Benzo[k]fluoranthene	ND	1.288 ± 0.186
Benzo[a]pyrene	ND	1.855 ± 0.111
Indeno[1,2,3-cd]pyrene	ND	ND
Dibenz[a,h]anthracene	ND	ND
Benzo[ghi]perylene	ND	ND

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

Table 5: Mean concentration of the individual PAH (µg/gm) measured in winter at AL-nahrawan bricks factory using GC analysis.

	Surface soil	Depth soil
Compound	Mean ± Confidence interval	Mean ± Confidence interval
Naphthalene	12.069 ± 0.144	32.713±0.031
Acenaphthylene	ND	ND
Acenaphthene	9.484 ±1.092	7.484±0.125
Fluorene	7.515±0.745	2.831 ±0.165
Phenanthrene	ND	2.608 ±0.161
Anthracene	1.139±0.098	3.052 ± 0.124
Fluoranthene	ND	ND
Pyrene	ND	ND
Benzo[a]anthracene	2.445± 0.112	1.702± 0.032
Chrysene	ND	ND
Benzo[b]fluoranthene	1.725±0.060	3.575± 0.063
Benzo[k]fluoranthene	18.843± 0.047	ND
Benzo[a]pyrene	11.69±0.199	ND
Indeno[1,2,3-cd]pyrene	ND	ND
Dibenz[a,h]anthracene	ND	ND
Benzo[ghi]perylene	ND	ND

The results show that sixteen polycyclic aromatic hydrocarbons were spread at chosen location as shown in figures 5 and 6. The concentration of 16 PAHs were varied in the two seasons. The most abundant compound in the summer season were naphthalene, acenaphthene, fluorene, pyrene and benzo[a]anthracene while in the winter were naphthalene, acenaphthene, fluorine, benzo [k] fluoranthene, benzo[a]pyrene due to these compounds had higher environmen-

tal stability because they have high aromatic property (Hassan et al., 2013; Schleyer et al., 2001; Dewar, 1969).

The high concentration was naphthalene 195.078 (µg/gm) due to naphthalene was easily formed according to the mechanism (March 1992; Hess et al., 1971). The high concentration in the winter was benzo[k]fluoranthene 18.843 (µg/gm). The existence of some polycyclic aromatic compounds at AL-nahrawan bricks factory due to incomplete combustion of black oil as well as effect of metrological conditions at chosen site. The cli-mate in Iraq is hot, dusty in summer and cool dry in the winter. The most effect of precipitated of PAHs on the soil were humidity and dust because PAHs deposition on the particles suspended in atmosphere (Rajput and Lakhani, 2009, Aryal et al., 2005). The concentration of PAHs in summer higher than in winter as a result of requests the production of bricks leading to consumption more fuel and more emission of PAHs in the summer.

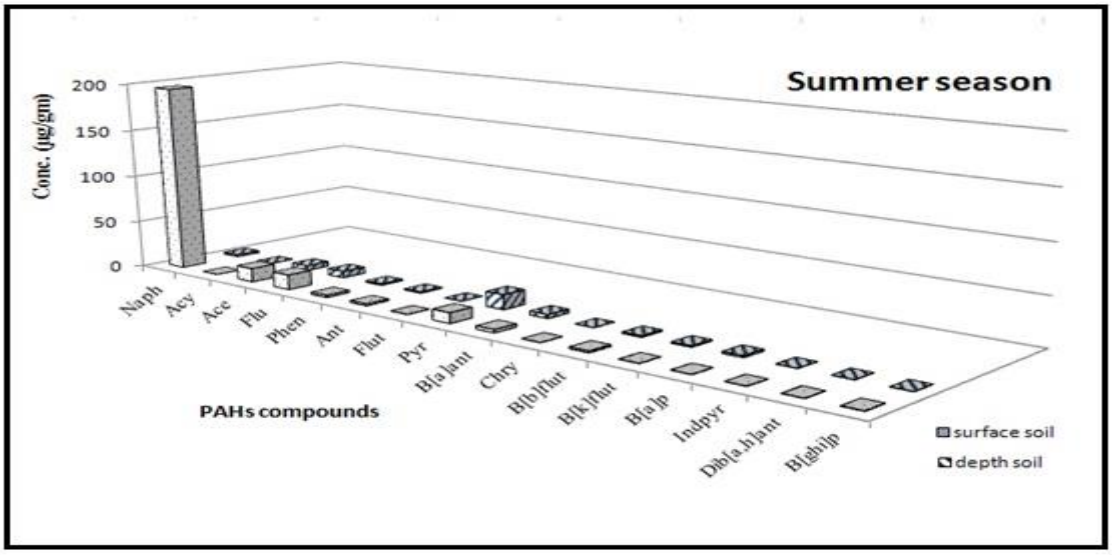

Figure 5: Mean concentrations of individual PAH in summer at AL-nahrawan bricks factory.

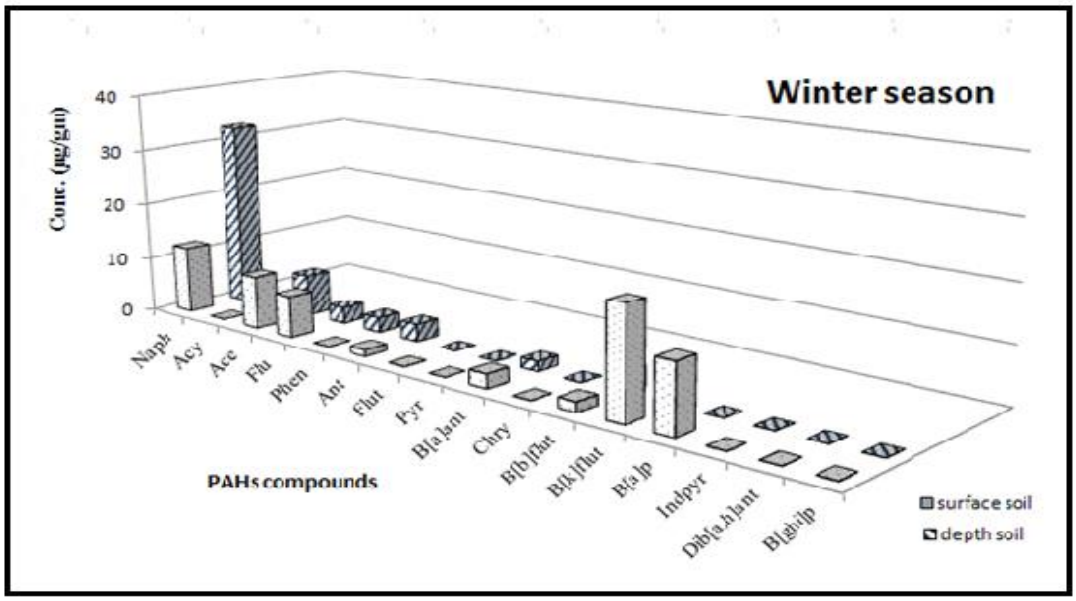

Figure 6: Mean concentrations of individual PAH in winter at AL-nahrawan bricks factory.

Conclusion

Sixteen polycyclic aromatic hydrocarbons were determined in soil samples at AL-nahrawan bricks factory by used GC apparatus. The concentration varied in the surface and depth soil as well as in the summer and winter seasons. The most polycyclic aromatic hydrocarbons speared were low molecular weight. The most abundant compound in the summer season was naphthalene.

REFERENCES

Aryal, R.K., Furumai, H., Nakajima, F. and Boller, M., Dynamic behavior of fractional suspended solids and particle-bound polycyclic aromatic hydrocarbons in highway runoff. *Water Research*, *39*(20):5126-5134 (2005).

Dewar, M.J.S., Molecular orbital theory of organic chemistry (1969).

Dong, C.D., Chen, C.F. and Chen, C.W., Determination of polycyclic aromatic hydrocarbons in industrial harbor sediments by GC-MS. *International journal of environmental research and public health*, *9*(6): 2175-2188 (2012).

Haleyur, N., Shahsavari, E., Mansur, A.A., Koshlaf, E., Morrison, P.D., Osborn, A.M. and Ball, A.S., Comparison of rapid solvent extraction systems for the GC–MS/MS characterization of polycyclic aromatic hydrocarbons in aged, contaminated soil. *MethodsX*, *3*:364-370 (2016).

Hassan, Y., Characterization of road side surface soil and road runoff water of Guwahati city with special emphasis on heavy metals (2014).

Hawthorne, S.B., Miller, D.J. and Kreitinger, J.P., Measurement of total polycyclic aromatic hydrocarbon concentrations in sediments and toxic units used for estimating risk to benthic invertebrates at manufactured gas plant sites. *Environmental toxicology and chemistry*, *25*(1) :287-296 (2006).

Hess Jr, B.A. and Schaad, L.J., Hueckel molecular orbital. pi. resonance energies. New approach. *Journal of the American Chemical Society 93*(2): 305-310 (1971).

Khan, M. and Ghouri, A.M., Environmental pollution: its effects on life and its remedies (2011).

Khan, Z., Troquet, J. and Vachelard, C., Sample preparation and analytical techniques for determination of polyaromatic hydrocarbons in soils. *International Journal of Environmental Science & Technology 2*(3): 275-286 (2005).

Lau, E.V., Gan, S. and Ng, H.K., Extraction techniques for polycyclic aromatic hydrocarbons in soils. *International journal of analytical chemistry*, *(2010)*.

March, J., *Advanced organic chemistry: reactions, mechanisms, and structure*. John Wiley & Sons, (1992).

Michigan, USA. *Environmental toxicology and chemistry*, *27*(2) :313-322 (2008).

Obini, U., Okafor, C.O. and J.N. Afiukwa, Determination of levels of polycyclic aromatic hydrocarbons in soil contaminated with spent motor Engine oil in Abakaliki Auto-Mechanic Village. *Journal of Applied Sciences and Environmental Management 17*(2):169-175 (2013)

Rajput, N. and Lakhani, A., Particle associated polycyclic aromatic hydrocarbons in urban air of Agra. *Indian J. of Radio & Space Physics*, 38: 98-104 *(2009).*

Robinson, S.D., Landrum, P.F., Van Hoof, P.L. and Eadie, B.J., Seasonal variation of polychlorinated biphenyl congeners in surficial sediment, trapped settling material, and suspended particulate material in Lake

Schleyer, P.V.R., Manoharan, M., Jiao, H. and F. Stahl, The acenes: is there a relationship between aromatic stabilization and reactivety?. *Organic letters 3*(23): 3643-3646 (2001).