Environmental Assessment of Polycyclic Aromatic Hydrocarbon Concentrations in soil at AL-zubaidiya Thermal Power Plant.

Thamera K. M. Al-Rudaini¹, Israa M. H. Almousawi*², Abdulkareem M. A. Al-Sammarraie²

¹Ministry of Science and Technology, Baghdad, Iraq. ²Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq.

E.mail: israa_mousawi@yahoo.com

Abstract. Polycyclic aromatic hydrocarbons (PAHs) were measured in soil samples, which collected for the period from January to August 2017, in Baghdad city, at AL-zubaidiya Thermal Power Plant. Soil samples were extracted by the soxhlet apparatus using mixture of acetone and hexane (1:1), and analyzed by GC/FID apparatus. The results show that the sixteen polycyclic aromatic hydrocarbon concentrations were varied in the two seasons. The most abundant compound in winter was naphthalene, while in summer season were naphthalene, acenaphthene, fluorene, pyrene and benzo[a]anthracene. The distribution of PAHs that have different aromatics ring, where the 2-rings are dominant in the winter season, while 2-rings, 3-rings, 4-rings are exists in summer season.

Key words: AL-zubaidiya Thermal Power Plant, PAHs, GC/FID

1. Introduction

Polycyclic aromatic hydrocarbons have two or more single or fused aromatic rings with a pair of carbon atoms shared between rings in their molecules. There are thousands of PAHs compounds in the environment but in practice PAHs analysis is restricted to the determination of 6 to 16 PAHs as priority pollutants, while some of these, e.g. benzo (a) pyrene, chrysene, benzo (a) anthracene are considered to be potential human carcinogens as shown in figure (1). [1-3]

The major source of PAHs is the incomplete combustion of organic material such as coal, oil and wood. Most of the PAHs are introduced into the soil from atmospheric decomposition after local and long-range transport, which is supported by the presence of PAHs in soil of regions remote from any industrial activity. Other potential sources of PAHs in environment include disposal from public sewage treatment, irrigation with coke oven effluent, leachate from bituminous coal storage sites, and use of soil compost and fertilizers. [4-5] This work includes collection of twelve soil samples from AL-zubaidiya thermal power plant at Baghdad city during period from January to Augusts 2017 to determine sixteen polycyclic aromatic hydrocarbons. Soil samples collected from surface and depth of chosen sites. Polycyclic aromatic hydrocarbons analyzed by GC/FID.
2. Experimental

2.1 Sampling site characteristics

The sites were chosen near the pollution source and around it to measure the PAHs. AL-zubaidiya power plant formed from six units, it is located at the western side of Tigris river and near AL-zubaidiya town, which is belonging to AL-kut government in south of Baghdad. It was operated in 2013 and the used fuel is gas oil.

The surface soil samples were collected using hand shovel and measuring tape. The monitoring of PAHs was focused on the surface soil and a depth of 30 cm.

2.2 Chemical and Standard material

Acetone (BDH, 99.8%) and hexane (BDH, 99.8%) were used for extraction of PAH from soil samples. The standard individual material polycyclic 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. Solutions of these compounds mixtures or single component) are soluble in methanol.
2.3 Standard solution

The retention time of the individual compounds (PAHs) were measured with range concentration (3-13) ppm. The target compounds PAHs were identified by comparing with retention time of standard compound. The final concentration of compounds PAHs were calculated from calibration curve and converted to µg/gm.

2.4 Sample Preparation and Extraction Method

Twelve samples were collected through measuring period. A 20 gm from soil sample was dried for four hours at 60 °C and grinded. Ground soil was put into the soxhlet apparatus using two solvent acetone and hexane (1:1) for about 15 hours [6]. The total volume of solvents extracted was 50 ml. The soxhlet extractor consisted of a 250 mL round-bottom flask, 50 mL extractor, condenser and water bath. After extraction, the extract was removed from the soxhlet apparatus and filtered by filter paper. Then the filtrate was left in air until dryness, dissolved in 5 ml methanol and filtered using micro filter. The solution was kept in glass container at low temperature before analysis.

2.5 GC analysis

The twelve soil samples were analyzed by GC apparatus (column, 5% phenyl, 95% methyl polysiloxane) to determine the concentration of sixteen PAHs compounds [7-8]. Detector temperature was kept at 300 °C. The transfer line and ion source temperature was 90 °C (hold for 1 min) to 150 °C (10 °C/min) then ramped to 300 °C (5 °C/ min) and final temperature was 300 °C (5 °C/ min, hold for 12 min). The analysis time for every sample was 50 minutes.

Result and Discussion

Evaluation of PAHs Concentration by Using GC/FID

The retention time (tR) and linearity equations of individual standard is summarized in table (1).

Table (1): The retention time (tR) and linearity equations of sixteen PAHs.

| Compound                  | Retention Time (tR) | Linearity Equations |
|---------------------------|---------------------|---------------------|
| 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 + 0.996     |
| 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      |
The selectivity of the method showed good separation and the peaks of the sixteen PAH fractions were distinct. The qualitative analysis was based on the comparison of retention times of target PAHs with retention times of standard compounds, while quantitative analysis was based on a linearity equation of the calibration curve. Figures (2-3) show some calibration curves of compounds, while figure (4) show the soil sample at chosen site.

![Figure 2: GC calibration curve of the standard pyrene.](image)

![Figure 3: GC calibration curve of the standard benzo (b) fluoranthene.](image)
Twelve soil samples were extracted and quantified for sixteen PAHs by using GC/FID apparatus for both winter and summer seasons. The average concentrations of individual PAHs in winter and summer seasons are listed in tables (2) and (3) respectively.

Table 2: Mean concentrations of the individual PAHs (µg/g) measured in winter at electric station using GC analysis.

| Compound                | Conc. of PAH on soil surface | Conc. of PAH in soil depth |
|-------------------------|------------------------------|----------------------------|
|                         | Mean ± Confidence Interval   | Mean ± Confidence Interval |
| 1 Naphthalene           | 14.161 ± 0.398               | 22.317 ± 0.042             |
| 2 Acenaphthylene        | ND                           | ND                         |
| 3 Acenaphthene          | ND                           | 7.243 ± 0.081              |
| 4 Fluorene              | ND                           | 8.309 ± 0.460              |
| 5 Phenanthrene          | 2.138 ± 0.094                | 1.549 ± 0.122              |
| 6 Anthracene            | 1.113 ± 0.012                | 0.543 ± 0.081              |
| 7 Fluoranthene          | ND                           | ND                         |
| 8 Pyrene                | ND                           | ND                         |
| 9 Benzo[a]anthracene    | 0.776 ± 0.032                | 1.055 ± 0.083              |
| 10 Chrysene             | ND                           | ND                         |
| 11 Benzo[b]fluoranthene | ND                           | ND                         |
| 12 Benzo[k]fluoranthene | 2.144 ± 0.082                | ND                         |
| 13 Benzo[a]pyrene       | 2.461 ± 0.344                | ND                         |
| 14 Indeno[1,2,3-cd]pyrene| ND                           | ND                         |
| 15 Dibenz[a,h]anthracene| ND                           | ND                         |
| 16 Benzo[ghi]perylene   | ND                           | ND                         |

* Mean ($\bar{X}$) when n=3 (µg/mg), confidence interval = $t \times \frac{s_{n-1}}{\sqrt{3}}$, degree of freedom (df) =2 and $t_{\text{tab,}k}=4.303$ for n=3 (No. of measurements). ND: not detected.
Table 3: Mean concentrations of the individual PAHs (µg/g) measured in summer at electric station using GC analysis.

| Compound              | Concentration on soil surface Mean ± Confidence interval | Concentration in soil depth Mean ± Confidence interval |
|-----------------------|--------------------------------------------------------|-------------------------------------------------------|
| 1 Naphthalene         | 6.130 ± 0.076                                          | 9.208 ± 0.006                                         |
| 2 Acenaphthylene      | 1.912 ± 0.093                                          | 1.498 ± 0.188                                         |
| 3 Acenaphthene        | 7.627 ± 0.258                                          | 8.499 ± 0.278                                         |
| 4 Fluorene            | 7.493 ± 0.540                                          | 6.801 ± 0.406                                         |
| 5 Phenanthrene        | 1.279 ± 0.663                                          | 1.608 ± 0.479                                         |
| 6 Anthracene          | 0.581 ± 0.025                                          | 1.261 ± 0.621                                         |
| 7 Fluoranthene        | 1.177 ± 0.060                                          | ND                                                    |
| 8 Pyrene              | 12.124 ± 0.306                                         | 18.485 ± 0.882                                        |
| 9 Benzo[a]anthracene  | 3.551 ± 0.993                                          | 4.108 ± 0.000                                         |
| 10 Chrysene           | ND                                                     | ND                                                    |
| 11 Benzo[b]fluoranthene| 1.263 ± 0.615                                         | 0.634 ± 0.415                                         |
| 12 Benzo[k]fluoranthene| ND                                                     | ND                                                    |
| 13 Benzo[a]pyrene     | 2.413 ± 0.740                                          | 1.857 ± 0.134                                         |
| 14 Indeno[1,2,3-cd]pyrene | ND                                                     | ND                                                    |
| 15 Dibenz[a,h]anthracene| ND                                                     | ND                                                    |
| 16 Benzo[ghi]perylene | ND                                                     | ND                                                    |

The results show that the sixteen polycyclic aromatic hydrocarbons were spread at chosen location as shown in figures (5) and (6).

Figure (5): Mean concentrations of individual PAHs in winter at AL-zubaidiya thermal power plant.
Figure (6): Mean concentrations of individual PAHs in summer at AL-zubaidiya thermal power plant.

The concentrations of 16 PAHs were varied in the two seasons. The most abundant compound in winter were naphthalene, while in summer season were naphthalene, acenaphthene, fluorene, pyrene and benzo[a]anthracene.

The results show most of the sixteen PAHs compounds were spread on the depth more than surface soil. The high concentration of naphthalene (14.161) µg/g was due to its mechanism that easily formed [9-10]. On the other hand pyrene was the higher concentration in winter (12.124) µg/g. The existence of some polycyclic aromatic compounds at AL-zubaidiya electric station is due to incomplete combustion of gas oil as well as effect of meteorological conditions at chosen site. The concentrations of PAHs in summer was (45.553) µg/g higher than in winter (22.793) µg/g due to the climate which is hot and dusty in summer that led to increase the deposition of compounds from atmosphere to soil [11-13].

The distribution of PAHs that have different aromatics rings in the chosen site is illustrated in figure (7). The 2-rings are dominant in the winter season, while 2-rings, 3-rings, 4-rings are exists in summer season.
Figure (7): The mean concentration of 2-rings, 3-rings, 4-rings, 5-rings and 6-rings PAHs in soil sample A. winter and B. summer at AL-zubiadiya thermal power plant.

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