Concentration of some Polycyclic Aromatic Hydrocarbons in soil samples of Kirkuk province, Iraq

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Abstract

In order to evaluate the quantity of twelve PAHs (Naphthalene, Tetraphan and Acenaphthyene Fluorene, Phenanthrene, Anthracene, Pyrene, Benzo [a] Anthracene, Ovalene, Chrysene, Benzo [a] fluoranthen and DiBenzo [ah] Anthracene) in the soil samples from Kirkuk province, seven sites (Ras El-Gesr, Benja Ali, Wahed Hozeran, North Oil Company (NOC), Lillian, Kubri and Chimom) were selected using Gas Chromatography (GC) during the autumn 2017 and winter 2018. The results showed that the highest concentration of individual hydrocarbons during the autumn season was for the Acenaphthylene compound in the NOC site 31.19 µg/kg, and for Naphthalene compound, was 100.543 µg/kg. The NOC recorded the highest concentration of total hydrocarbons 891.65 µg/kg. For the winter season, the highest concentration of polycyclic aromatic hydrocarbons was recorded for the Fluorene compound at the NOC site 79.19 µg/kg. Fluorene and Naphthalene compounds achieved the highest averages for the season (43.24 and 42.984 µg/kg) respectively, and recorded the location of the NOC, the highest summation of total hydrocarbons amounted to 609.77 µg/kg.

1. Introduction

PAHs in the atmosphere are constantly deposited into the ground by dry or wet deposition processes. Some of these compounds are from near sources, such as car exhausts from nearby roads. Other PAHs are from distant sources and transported over different distances through the air. At the same time, PAHs can be added to the soil if soil materials contain them. When PAHs and other compounds are deposited on the surface of the earth, they can become attached to the soil molecules [1, 2]. The most important factors affecting the movement of PAHs in the soil are the size of the attached particles and the size of the soil pores (this throat or pores can be defined as small spaces between individual minutes of soil) [3]. If the particles in which the PAHs cannot move through the soil, the movement of these compounds will be limited because they tend to be absorbed (impregnated) into these particles. The soil contains measurable quantities of PAHs, primarily from airborne outputs. Reported levels of PAHs in soil near oil refineries are reported to 200,000 micrograms / kg of dehydrated soils. Levels of soil samples obtained near cities and areas with heavy traffic are usually less than 2,000 micrograms/ kg [4]. Thirteen of PAHs were measured in 46 soil samples from San Nicolás, an area that includes a brick manufacturing company in central Mexico. Total concentrations of PAHs ranged from 7 ng/ g to 1384 ng/ g with an average value of 220 ng/ g. Naphthalene (Nap) was more abundant followed by
Fluorene (Flu), chrysene (Chry), benzo [a] anthracene (BaA) and DiBenzo [a, h] anthracene (DahA). The average samples of naphthalene were 374 ng / g. It was also found that about 52% to 76% of the soil of San Nicolas had higher PAHs than those considered normal or non-serious for residential use. In addition, the total concentration of benzo [a] Pyrene in the soil of San Nicolas was higher than the upper limit. Of particular concern is the high volume of DahA and BaP, which are high-potential PAHs to cause cancer. All these factors mean a potential cancer risk for the exposed populations in San Nicolas [5].

In the study of [6] for the purpose of evaluating the levels of PAHs in the air of the thermal power plant in Baghdad, they indicated that the highest concentration of these compounds was for Naphthalene, with an average of 72-1573.5 ng / m3 during the summer season, 14.387 to 36.65 ng / m3 during the winter season.

The degradation of PAHs in the environment includes: biodegradation [7, 8], photolysis, chemical oxidation, adsorption of soil particles, leaching and bioaccumulation [9]. Each of these processes affects different PAHs in different ways. This is mainly due to the fact that each compound of the PAHs compounds has a unique structure and a range of physical, chemical and biological properties. On the other hand, the removal of these compounds from the atmosphere was studied by [10-12]. The gas phase of hydrocarbons is more efficiently removed from the atmosphere in colder conditions than in warm conditions [13, 14].

In the study [15] at north of Nijif city in Iraq, the total concentration of sixteen polycyclic aromatic hydrocarbons was 49.9 to 986.4 μg/ kg, by average 587.2 μg/ kg. The most abundant polycyclic aromatic hydrocarbon compound in the surface soil of the study area was Fluorene, followed by Acenaphthylene, Naphthalene, Chrysene, Phenanthrene, Benzo (b)fluoranthene, Fluoranthene, Benzo (a) anthracene, Benzo (a) Pyrene, Benzo (g, h, i) perylene and Dibenzo (a, h) anthracene, Indeno (1,2,3-cd) Pyrene, Pyrene, Acenaphthene, Anthracene and Benzo (k) fluoranthene. Syed et al. [16] noted that the total concentration of 15 hydrocarbon compounds studied in soil A and O for a number of Chinese forest soils ranged from 168-220 ng / g. The current study aims at evaluating the concentrations of PAHs in soil samples of seven different sites within Kirkuk provinve during two different periods.

2. Materials and methods of study

2.1. Selection of study areas

The current study included a field survey of seven different sites of Kirkuk province showing intersections in GPS Table (1) during the autumn 2017 (average of September, October and November) and winter 2018 seasons (average of December, January and February). Soil samples analyzed for detecting twelve compounds of polycyclic aromatic hydrocarbons. These sites and their characteristics are: first site – Ras El-Gesr (center of city): - It represents the crowded site with commercial activity. Second site - Benja Ali (center of city): -It is residential and contains a well-oil burning in the eastern side of the city. Third site - Wahed Hozeran (center of city): - represents the southwestern part of the city. Fourth - North Oil Company: - Located northwest of Kirkuk and includes a number of oil refining and refining facilities, in addition to a number of oil fields. The fifth site - Lillian: - includes Kirkuk cement factory and is located southeast of Kirkuk. The sixth site - Kubri: - is located north of Kirkuk with high anthropogenic activity. Site seventh - Chimen area (as control): - A rural area free of industrial facilities, located northeast of Kirkuk.

| No. | Site                          | North     | South     |
|-----|-------------------------------|-----------|-----------|
| 1   | Ras El-Gesr (center of city)  | 35.46˚    | 44.39˚    |
| 2   | Benja Ali (center of city)    | 35.41˚    | 44.43˚    |
| 3   | Wahed Hozeran (center of city)| 35.40˚    | 44.34˚    |
| 4   | North Oil Company             | 35.55˚    | 44.36˚    |
2.2. Soil sampling collection
Soil samples were taken from each of the seven selected sites from the upper soil layer of depth of 0-10 cm using a stainless steel drill. The soil samples were placed in foil aluminum paper [17]. Soil samples were cleaned, dried on paper, labeled and breezed at -20°C till analysis. The samples were then sieved through 2mm sieve (EPA method 3052) to remove coarse particles (USEPA, 1995) [18] before extraction. Laboratory work extraction of samples was done as described by WMO / IOC, 1989 [19]. 10 g of soil drying was taken and homogeneous in a stainless steel bowl, then about 25 mL of acetone was added in the flask and mix with hand for five minutes. The sample is then placed in a dark, cool place overnight and then mixed with a shaker for an hour. The solution is separated and placed in a darkened glass container. This process is repeated three times. The solutions obtained from the previous step were then transferred and placed in centrifuge at 2500 rpm for 5 minutes. 50 ml hexane and 100 ml of free ion water were added to solution, two layers will be formed, the lower layer will neglect while the upper layer will be collected and add 50 ml of KOH will added. The volume is reduced to 10 mL by the rotary evaporator device, transferred to the silica gel column, dried and dissolved in 1 ml of Acetonitrile: Methanol at 90:10 and kept until measurement.

2.3. Aromatic hydrocarbons included in the study
The device has been calibrated using standard of twelve compounds of polycyclic aromatic hydrocarbons solution, as shown in Table 2.

|   |   |   |   |
|---|---|---|---|
| 5 | Lillan | 35.34° | 44.47° |
| 6 | Kubri | 35.75° | 44.14° |
| 7 | Chimen | 35.31° | 44.19° |

Figure 1. Map shows studied sites in Kirkuk province.
2.4. Calculations and statistical analysis
PAHs were analyzed using a Chromatography Gas Model 2010-Shimadzo and FID ionized flame detector and used a column-type capillary 30 (30-SE) 07 meters long and 7200 mm in diameter to separate compounds according to the following conditions [20]. The temperature of the injection area was 280 °C. Reagent temperature was 330 °C. The temperature of the separation column starts from 100 °C and stays for 3 minutes and then increases 10 degrees every minute until reach 310 °C. After the extraction process is completed, 1μl of the extract is injected with a device-type syringe (10 as 1701 Hamilton), with a capacity of 10μl, and the injection is performed. Polycyclic aromatic hydrocarbons separated in the chromatogram of each sample with a standard chromatogram retention time, the concentrations of PAHs were calculated according to the following equation [21].

\[
C = \frac{\text{Cst} \times \text{Asam} \times \text{D.F}}{\text{Ast} \times \text{Wt}}
\]

Whereas C = concentration to be calculated for hydrocarbons per million. Cst = the standard concentration of the compound and equal 10. Asam = calculated area of peak. Ast = The standard area of peak is fixed for all compounds and is (15436). D.F = dilution factor equals 10. Wt = weight of sample.

| No. | Compounds             | simple | No. of Ring | R. Time |
|-----|-----------------------|--------|-------------|---------|
| 1   | Naphthalene           | Nap    | 2           | 7.962   |
| 2   | Tetraphan             | Tet    | 4           | 9.99    |
| 3   | Acenaphthylene        | Acy    | 3           | 11.11   |
| 4   | Fluorene              | Flu    | 4           | 11.836  |
| 5   | Phenanthrene          | Phe    | 3           | 13.801  |
| 6   | Anthracene            | Ant    | 3           | 15.834  |
| 7   | Pyrene                | Pyr    | 4           | 16.739  |
| 8   | Benzo[a]Anthracene    | B[a]Ant| 4           | 16.861  |
| 9   | Ovalene               | Ova    | 10          | 17.545  |
| 10  | Chrysene              | Chry   | 4           | 18.171  |
| 11  | Benzo[a]fluoranthene  | BaF    | 5           | 18.723  |
| 12  | DiBenzo[ah]Anthracene | DAH    | 5           | 19828   |

2.5. Statistical analysis
The results were statistically analyzed according to the statistical program (SPSS). All data were treated with the analysis for significance differences among sites and study period using Duncan Multi-Range Test. The possible sources (Pyrogenic or Petrogenic origin) in soil samples may be assessed by the ratio of individual PAHs compounds [22], who stated that these ratios were based on the use of PAHs from the molecular mass 178 and 202. These ratios are used in the present study: (a) Ant / Ant + Phe: - According to this ratio it was assumed that the resulting values that are less than 0.1 indicate the petrogenic source of PAHs, while more than 0.1 to PAHs out of combustion. (B) Fluo / Fluo + Pyr: - It is assumed that the ratios ranging from 0.4 to 0.5 refer to pyrogenicsource, and the ratios of less than 0.4 refer to petrogenic sources. The ratio greater than 0.5 indicate the burning of wood and coal. Inengtie et al., [23] also reported that the ratio of Australian crude oil is less than 0.4, and that some oils have very high proportions of fluoranthene. (C) BaA / BaA + Chry: - Assume that the ratio less than 0.2 referred to petrogenic origin, and the ratios of 0.2 to 0.35 with mixed sources. The ratio greater than 0.35 is due to combustion.
3. Results and discussion

Figures (2, 3, 4) and table (3) shows the concentrations of the twelve individual hydrocarbons during the autumn of the seven sites under study. The highest concentration of three-ring Acenaphthylene at the North Oil Company's site was 131.9 μg / kg, followed by a four-ring Pyrene with a concentration of 130 μg / kg. Naphthalene was, with high concentrations at all sites except for the control site (Chemin), which was near to zero, with a maximum concentration of 128.6 μg / kg. The results of seven site, North Oil Company were significantly higher for all compounds, followed by Kobri and Lillan sites with significant industrial activity. Barrán-Berdón at al., [5] were obtained total concentrations of PAHs in the soil samples from 7 μg / kg to 1384 μg / kg with an average of 220 μg / Kg. They noted that Naphthalene is more abundant followed by Fluorene, Chrysene, Benzo [a] Anthracene and Dibenzo [a, h] Anthracene. The average samples of Naphthalene were 374 μg / kg. The highest mean Naphthalene compound was 100.543 μg / kg and significantly higher than the average of the other compounds according to the results of the Duncan Multimodal Mean Test followed by Acryaphthylene triacile (67.414 μg / kg), significant for some compounds and not significant for other compounds according to the Duncan Multi-Range Test. The site of the North Oil Company was recorded the highest concentration of total hydrocarbons with a value of 891.65 μg / kg, accounting for 25% of the total hydrocarbons. The availability of low molecular PAHs as Naphthalene compound may be due to their contribution to the formation of SOA molecules resulting from ozone degradation, which slowly characterizes evaporation and elevation of their viscosity and ensures longer atmospheric life. Increased viscosity provides a shield that protects PAHs from chemical degradation and evaporation, allowing the transport of toxic pollutants to distant ranges [24].

**Figure 2.** Individual hydrocarbon concentrations in the soil for the seven sites during the autumn season.
Figure 3. Means of PAHs in soil as average of seven sites during the autumn

Figure 4. Total hydrocarbon concentrations in soil of seven sites during autumn.

Table 3. Concentrations of the compounds, their mean and their aggregates in the soil samples of the study sites during the autumn season.

| Sites Compounds | Ras El-Gesr | Benja Ali | Wahed Hozera | North Oil Company | Lillian | Kubri | Chemin | Means of compounds |
|-----------------|------------|-----------|--------------|-------------------|--------|-------|--------|-------------------|
| Naph            | e106.6     | d117.6    | f94.7        | a128.6            | c123.3 | b125.7| g7.3   | a100.519          |
| Tet             | e33.01     | d39.27    | f16.28       | a77.92            | b47.23 | c46.26| g10.32 | de38.613          |
| Acy             | e47.6      | d51.2     | f40.7        | a131.9            | c67.3  | b95.5 | g37.7  | b67.426           |
| Flu             | e33.76     | d41.99    | f23.47       | a92.91            | b63.81 | c56.8 | g9.11  | cd45.979          |
| Phe             | e43.92     | d49.35    | f35.17       | a54.89            | c52.28 | b53.56| g8.89  | d42.58            |
| Ant             | e18.01     | d18.11    | f16.28       | a44.94            | c35.84 | b36.89| g1.61  | ef24.526          |
| Pyr             | e45.9      | d58.9     | f43.6        | a130              | c79.5  | b84.6 | g6.7   | b64.169           |
For the winter season, Figure (5, 6, 7) and Table (4) show the results of PAHs during winter. The highest concentration of PAHs was recorded for the Fluorine compound in the North Oil Company’s site of 79.19 μg / kg, followed by Acenaphthylene and Naphthalene with a concentration of 69.94 and 68.23 μg / kg respectively. The lowest concentration was for Pyrene and Benzo [a] Anthracene, at some sites. It also noted that the high concentrations were recorded for all PAHs at North Oil Company site except Benzo [a] Anthracene, which exceeded significantly for other sites. For average PAHs, Naphthalene and Fluorene compounds recorded the highest mean at soil samples during the winter with concentrations of 43.24 and 42.984 μg / kg respectively according to the results of the Duncan Multimode Intermediate Test.

![Figure 5. Individual hydrocarbon concentrations in soil for the seven sites during the winter season.](image-url)
The site of the North Oil Company was with highest concentration of 609.77 μg / kg, accounting for 28% Total PAHs of soil samples during the winter, while the differences were evident between the other sites. The control site (Chemin) recorded the lowest total hydrocarbons of 77.42 μg / kg, accounting for 4% of total PAHs in the soil samples during the winter season. Previous studies have found by Abed et al., [15] at north Biji City in Iraq showed that the total concentration of 16 polycyclic aromatic hydrocarbons ranged from 49.9 to 986.4 μg / kg at 587.2 μg / kg. The most abundant polycyclic aromatic hydrocarbon compound in the surface soil of the study area was Fluorene followed by Acenaphylene and Naphthalene.
Table 4. Mean concentrations of PAHs in the soil samples of the study sites during winter.

| Sites compounds | Ras El-Gesr | Benja Ali | Wahed Hozeran | North Oil Company | Lilan | Kubri | Chemin | Means of compounds of compounds |
|-----------------|-------------|-----------|---------------|-------------------|-------|-------|--------|--------------------------------|
| Naph            | e45.9       | d46.56    | f23.63        | a68.23            | c47.57| b49.54| g21.25 | a43.24                        |
| Tet             | e4.45       | d14.45    | f3.27         | a35.71            | c41.35| b56.94| g2.51  | c22.383                       |
| Acy             | e11.64      | d12.49    | f8.73         | a69.94            | c14.11| b19.51| g1.19  | c19.659                       |
| Flu             | e38.11      | d42.42    | f36.82        | a79.19            | c47.03| b49.73| g7.59  | a42.983                       |
| Phe             | e20.19      | d21.24    | f19.5         | a66.71            | c21.674| b33.62| g14.27 | bc28.172                      |
| Ant             | e14.89      | d31.34    | f14.56        | a58.38            | c49.13| b53.38| g4.11  | abc32.256                     |
| Pyr             | e2.58       | d3.99     | f1.79         | a5.78             | c4.89 | b4.95 | g1.08  | d3.58                         |
| B[a]A            | f0.09       | d0.99     | e0.8          | b2.32             | c1.96 | a2.34 | g0.05  | d1.221                        |
| Ova             | e26.71      | d31.47    | f24.74        | a47.19            | c33.57| b41.69| g3.54  | bc29.844                      |
| Chry            | e41.69      | d43.35    | f22.97        | a48.89            | c43.86| b46.38| g20.06 | ab38.171                      |
| Bbf             | e12.06      | d17.95    | f10.02        | a58.11            | c29.04| b46.42| g1.74  | bc25.049                      |
| dBA             | e1.48       | d6.77     | f0.22         | a69.32            | c13.04| b50.68| g0.03  | c20.22                        |
| Total PAHs      | 219.79      | 273.02    | 167.05        | 609.77            | 347.224| 455.18| 77.42  |                               |

- Values followed by the same letter are not different from each other morally.

The results of the PAH concentrations in the soil samples during the two seasons of the study were summarized in Table 5. The highest concentration was recorded for Naphthalene during the autumn, which was 100.519 μg / kg with an mean concentration of 71.879 μg / kg and shoes significantly different with all other compounds. Seasonal averages show that the autumn season achieved the highest rate of 42.791 μg / kg, significantly different from the winter, according to the results of the multimodal Duncan method. The results of standard deviation showed a high dispersion between the sites for the concentration of each compound, where it is noted that all the mean of the compounds were significantly less than zero compared to their standard deviation values during the two seasons of study, except for the average of the two compounds Acenaphthylene during the autumn season and DiBenzo[ah] Anthracene during the winter season.

Table 5. Mean ± SD of 12 PAHs during autumn and winter for studied soil samples.

| seasons compounds | Autumn        | Winter        | Means of compounds |
|-------------------|---------------|---------------|--------------------|
| Naph              | a100.519±39.630| cd43.24±14.972| a71.879            |
| Tet               | cde38.61±20.732| d-g28.38±20.269| bcd33.498          |
| Acy               | b67.42±32.070 | f-i19.659±21.163| bc43.542          |
| Flu               | c45.97±25.826 | cd42.98±19.594| b44.481           |
| Phe               | cd42.58±15.136| d-g28.172±16.636| bcd35.376          |
| Ant               | efg24.52±14.012| c-g32.25±20.076| de28.391           |
| Pyr               | b64.16±36.003 | ij3.58±1.650 | bcd33.874          |
| B[a]A             | b61.43±19.900 | j1.22±0.917 | de31.327           |
| Ova               | g-j15.71±13.370| c-f33.84±13.014| de24.778           |
| Chry              | hij5.33±4.669 | cde38.17±10.777| ef21.754           |
For the sources of PAHs, it is observed that, by application of weight equations according to molecular weight and the phenomenon in Table (6), Ant/(Ant+Phe) showed that PAHs were the source of combustion at all sites and studied periods. The results for Flu/(Flu+Pyr) showed that the source of the compounds was the pyrogenic source at all sites during the autumn, where the values ranged from 0.4 to 0.5, except for Wahid Hozeran site in the city center was petrogenic source, the value of less than 0.4, during the winter season, the ratios showed that the compounds were sourced from the burning of natural materials (weeds, trees, coal) and all the sites, worth more than 0.5. for B[a]A/(B[a]A+Chry) In the autumn season, the values of the PAHs were more than 0.35, wherefore may be due to combustion. During the winter season, the values of these compounds were petroleum All sites, with values of less than 0.2. Bayowa [25] states that the PAHs in the soil samples were oil-based as well as the combustion of oil, timber and coal during the dry and rainy seasons. Abed et al. [15] noted that burning fossil fuels and burning plants are the main sources of PAHs in the soil samples they studied.

Table 6. Ratios of some individual PAHs for studied soil samples.

| Ratio       | Season sites | Ant/(Ant+Phe) | Flu/(Flu+Pyr) | B[a]A/(B[a]A+Chry) |
|-------------|--------------|---------------|---------------|--------------------|
|             | Autumn | Winter | Autumn | Winter | Autumn | Winter |
| Ras El-Gesr | 0.29   | 0.424  | 0.423  | 0.936  | 0.960  | 0.002  |
| Benja Ali   | 0.268  | 0.596  | 0.416  | 0.914  | 0.966  | 0.022  |
| Wahed Hozeran | 0.316 | 0.427  | 0.349  | 0.953  | 0.974  | 0.033  |
| North Oil Company | 0.450 | 0.466  | 0.416  | 0.932  | 0.884  | 0.045  |
| Lillan      | 0.406  | 0.693  | 0.445  | 0.905  | 0.883  | 0.043  |
| Kubri       | 0.407  | 0.613  | 0.402  | 0.909  | 0.889  | 0.048  |
| Chemin      | 0.153  | 0.223  | 0.576  | 0.875  | 0.993  | 0.002  |

The results of the study indicate that some soil samples contained relatively high concentrations of polycyclic aromatic hydrocarbons, especially at sites near to the sources of pollution, as North Oil Company site and the Kobrī, which includes oil refining factories, And the site of Lillan, which includes the Kirkuk cement factory. Bayowa [25] states that 90% of the polycyclic aromatic hydrocarbons in the soil have a half-life longer than in the air and the plant. In the study of Ana et al [26] in Nigeria's coastal areas, concentrations of PAHs were obtained in the soils of the sites. The industrial giant is up to three times what it is in smaller industrial sites. As for the seasons of the study, the concentration of these compounds during the autumn was higher than in the winter. This is related to the physical and chemical properties of these compounds and their impact on environmental factors. Most of the researchers proved that the concentrations of these compounds in warm climates may due to the availability of the internal causes of movement by stirring electrons inside molecules, and the external movement associated with wind, and then the accumulation of these compounds and sedimentation to the soil by different sedimentation ways Bayowa [25], which found in high levels during the dry season than in the rainy season. During the winter, due to increased humidity, the degradation of these compounds is increased by biological, physical and chemical ways [27], Dandie et al [28], Fredslund et al [29] Who stated that bacteria can decompose any PAHs. These results are consistent with [9, 13, 14]. Musa Bandowe et al. [4] and Barrán-Berdón et al., [5], Afaj et al., [6] Abed et al., [15] and Syed et al. [16].

- Values followed by the same letter are not different from each other morally.
4. **Conclusion**

We concluded that in winter, Fluorene was the most abundant compound followed by Naphthalene, and according to the different individual PAHs ratios, the origin of PAHs at soil samples was from pyrogenic and petrogenic sources. We recommend for further future studies to determine the non-point sources of PAHs in soil. Toxicological studies should be done to determine the impact of these compounds on human health.

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