



Evaluation of Surface Soils Contamination by Polycyclic Aromatic Hydrocarbons of Selected Samples in Al-Diwaniya City, Iraq

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Abstract

The concentrations and spatial distribution of thirteen polycyclic aromatic hydrocarbons from soil have been investigated in four regions located in Al-Diwaniya city, Iraq. Sechelt extractions is used to extract PAHs compounds from all samples, gas chromatography was used to determine the PAHs concentration in all samples. The total concentrations of thirteen PAHs were ranged from 4.46ng.g⁻¹ in site one to 17.24 ng.g⁻¹ in site three of dry weight. The PAHs compounds those consist of four to six fused aromatic rings represent the majority among other PAHs in soil samples.

Keywords: *Al-Diwaniyah pollution, Contamination with PAHs, Extraction of PAHs from soil, Soil pollution, PAHs in Iraqi soil.*

Introduction

Poly nuclear aromatic hydrocarbons or polycyclic aromatic hydrocarbons (PAHs) are organic compounds that consist of two or more fused aromatic rings [1]. They are income to our environment via by-products of incomplete combustion and pyrolysis of all organic matter in addition to the biogenic formation, volcanic eruptions [2]. Pollution with these compounds in soil is differing from air and water pollution in several ways. In air, most organic pollutants are decomposed by reaction with hydroxyl-radicals, and then posse's shorter half-lives in air than in both soil and water. In addition to, air and water may combine with contaminants, leading to the dilution of the PAH compounds into greater quantities and being transported to other portions of the environment. Nevertheless, in soil and sediments, where PAHs are adhesive with components of the soil and sediments, dilution, transport and degradation are being limited [3].

Most PAHs compounds are classified as mutagens and carcinogens; they are common in the water, soil and air [4]. The compounds of PAHs those posses' two fused aromatic

rings they are frequently have high stabilization in an environment due to their stability of chemical structure and hydrophobicity nature. These compounds are less soluble and can absorb by soil fragments, particularly in organic soil [5]. The soils type and properties such as contents of organic compounds play the role of the most important in adsorption of PAHs compounds in soils [6]. Owing to recalcitrant, hydrophobic, and bio accumulating characteristics, PAHs compounds are adsorbed strongly on biota and suspended particulates, and accumulated in sediment and soil, resulting in serious soil pollution problems. Many of them are carcinogenic and toxic [7-9], and 16 PAHs are listed by the United State Environmental Pollution Agency as priority pollutants [10].

While not as active a carcinogen compound as Benzo [a] Pyrene [11], Pyrene is an important mutagen spread in polluted soils [12]. Several previous studies were focused about assessment of PAHs compounds [13-17]. A lot of methods were studied the degradation of some compounds of PAHs using UV light

with catalysts [18, 19] and by Fenton processes [20]. This study aims to evaluate the pollution of selected surface soil samples from Al-Diwaniya Province.

Experimental Part

Soil Samples

All samples in this study are collected of surface soil from four regions in Al-Diwaniya city there are: north of city (S1), south of city (S2), west of city (S3) and east of city (S4). These samples were collected in spring of 2015. At each site, the surface sample of soil was taken (top 10 cm)[21]. The collected samples have been dealt with dry air after handling it's to the lab during three hours. The dried soil samples were discharged to pass during sieve and homogenized, and then samples were kept up in 4°C. All containers of samples and glasses staff were completely washed using detergent follow up by rinsing

with distilled water then with acetone. Samples were kept in oven at heating temperature 120 overnight. To void pollution of the samples, several syringes and glassware were used [15].

Chemical and Reagents

The standard solution of EPA 525PAHs mixture-A was purchased from Supelco. The mixture is consisting of:

Acenaphthylene, Phenanthrene, Chrysene, Benz (a) anthracene, Benzo (b) flouremthene, Benzo (ghi) perylene, Fluorene, Anthracene, Indeno (1,2,3-cd)pyrene, Pyrene, Benzo(k) flouremthene, Benzo(a)pyrene, and Dibenz (a,h) anthracene, table 1, illustrate composition of individual PAHs and their selected properties [3]. This standard was stored in refrigerator at 4°C, and kept away from light. Solvents were supplied from Sigma Aldrich.

Table 1: Selected properties of PAHs

Compound	Number frings	Molecular weight	Aqueous solubility (mg/l)	Vapor Press. (Pa)
Acenaphthylene	3	152	16.00000	9.0x10 ⁻¹
Fluorene	3	166	1.90000	9.0 x10 ⁻²
Phenanthrene	3	178	1.10000	2.0 x10 ⁻²
Anthracene	3	178	0.04500	1.0 x10 ⁻³
Pyrene	4	202	0.13000	6.0 x10 ⁻⁴
Benz[a]anthracene	4	228	0.01100	2.8 x10 ⁻⁵
Chrysene	4	228	0.00600	5.7 x10 ⁻⁷
Benzo[b]fluoranthene	5	252	0.00150	-
Benzo[k]fluoranthene	5	252	0.00080	5.2 x10 ⁻⁸
Benzo[a]pyrene	5	252	0.00380	7.0 x10 ⁻⁷
Dibenzo[a,h]anthracene	5	278	0.00060	3.7 x10 ⁻¹⁰
Indeno[1,2,3-cd]pyrene	6	276	0.00019	-
Benzo[ghi]perylene	6	276	0.00026	1.4 x10 ⁻⁸

Extraction Procedure

Ten grams of samples were weighed exactly and added to two grams of anhydrous sodium sulfate. PAHs compounds were extracted using Sechelt for twenty four hours with 160 mL of dichloromethane/hexane solvents (9:7 v/v). Rotary evaporator was used to overcome of the solvents and to minimize the volume of mixture to one m L.

Analysis Conditions

The extracted samples finally analyzed by gas chromatography (GC) Shimadzu/2014 split less mode injector was applied for all samples, HP-5 capillary column: (30 m × internal diameter 0.28 mm × Film thickness 0.25 μm). FID detector was used in this study. The carrier gas was nitrogen at flow rate 1 mL/min, while oven temperature was programmed as follow:

to increase from 50 °C (2 min) to 200 °C (2 min) at heating rate 20 °C/min, to 240 °C (2 min) at heating rate 5 °C/min and to 290 °C at heating rate 3 °C/min and then held for 15 min. The injector and detector temperatures were 275 and 300 °C, respectively [15].

Results and Discussion

Ten compounds of thirteen of PAHs were detected in soil samples (table 2), among which Pyrene was the highest concentration of PAHs compounds 5.36 ng.g⁻¹ while three compounds were not detected: Fluorine, Anthracite and Benz [a] Anthracite in all four sampling regions. Previous confirmation states that the potential carcinogenic of PAHs compounds are restricted with following PAHs: Benzo[a]pyrene, Indeno [1,2,3-cd] pyrene, Dibenz [a, h] anthracites, Chrysene, Benz[a] fnthracene, Benzo [b]

fluoranthene and Benzo[k]fluoranthene. This raises concerns of researchers about the potential risk to humans and the environment. Ratios of some PAHs such as Fluoranthene to Pyrene or the low molecular mass of PAHs to high molecular mass of PAHs are the two indexes that are most commonly used to assess the origin of PAHs compounds. This fact is attributed to the concentrations of Pyrene compound are much higher in fossil fuels and its byproducts than the concentration of Fluoranthene

compound. However the petrogenic pollution are predominated with low molecular mass of PAHs, while the pyrolytic pollution are characterized with high molecular mass of PAHs. Therefore, the ratio of Fluoranthene to Pyrene being less than one or the ratio of low molecular mass to high molecular mass being greater than one indicate pathogenic origin of PAHs pollutants, while the opposite case indicates pyrogenic origin of PAHs pollutants [22].

Table 2: Concentration of thirteen PAHs in ng.g⁻¹

Compound	S1	S2	S3	S4	Summation
Acenaphthylene	0.00	0.26	0.85	0.00	1.11
Fluorene	0.00	0.00	0.00	0.00	0.00
Phenanthrene	0.00	0.00	4.45	0.00	4.45
Anthracene	0.00	0.00	0.00	0.00	0.00
Pyrene	2.95	0.00	1.55	0.86	5.36
Benz[a]anthracene	0.00	0.00	0.00	0.00	0.00
Chrysene	0.00	0.00	1.54	2.02	3.56
Benzo[b]fluoranthene	0.00	0.00	2.52	0.00	2.52
Benzo[k]fluoranthene	1.51	0.00	0.00	0.00	1.51
Benzo[a]pyrene	0.00	0.00	2.97	0.00	2.97
Dibenzo[a,h]anthracene	0.00	1.39	0.00	1.83	3.22
Indeno[1,2,3-cd]pyrene	0.00	0.00	1.71	2.75	4.46
Benzo[ghi]perylene	0.00	0.00	1.74	0.00	1.74
Summation of PAHs	4.46	6.11	17.24	7.64	30.9

The PAHs compounds those consist of four to six fused aromatic rings represent the majority among other PAHs in soil samples, table (3), illustrates classification PAHs percentage according to the number of rings abundance in soil samples and their summation and percentage. This could due to

the higher biodegradation rate for low rings than high rings PAHs of soil bacteria in utilizing as energy [23]. Figure 1, shows PAHs that consist of five fused rings is the highest percentage of existence in all sample sites, while the PAHs consist of three rings is the lowest class.

Table 3: Percentage of PAHs in soil samples

No. of rings of PAHs	Summation	Percentage
Three rings	5.56	17.99%
Four rings	8.92	28.86%
Five rings	10.22	33.07%
Six rings	6.2	20.06%

The highest concentrations of PAHs was found at site 3 (west of city), this site is locate between two major roads connect Al-diwanayah city with both Al najaf and Alhilla governorates. The deposition of particulate associated PAHs compounds those emit from vehicles in addition to the existence of a lot of building block factories near this site, these factories release a huge amount of smoke to

air. The lowest concentrations of PAHs was detect in S1 locate at the north of Al-diwanayah city and is expected to receive a little impact of building block factories. The comparison between the levels of PAHs concentrations in this study with other studies in previous countries, we can reach to fact that is no pollution in this city [24].

In literature, pollution of soils with PAHs classified as four classes there are: heavily pollution when the summation of PAHs is higher than $1000 \mu\text{g.kg}^{-1}$, polluted soil when the summation of PAHs ranged between 600-

$1000 \mu\text{g.kg}^{-1}$, weakly polluted soil when the summation of PAHs ranged between 200-600 $\mu\text{g.kg}^{-1}$ and not polluted soil when the summation of PAHs is lower than 200 $\mu\text{g.kg}^{-1}$ [25, 26].

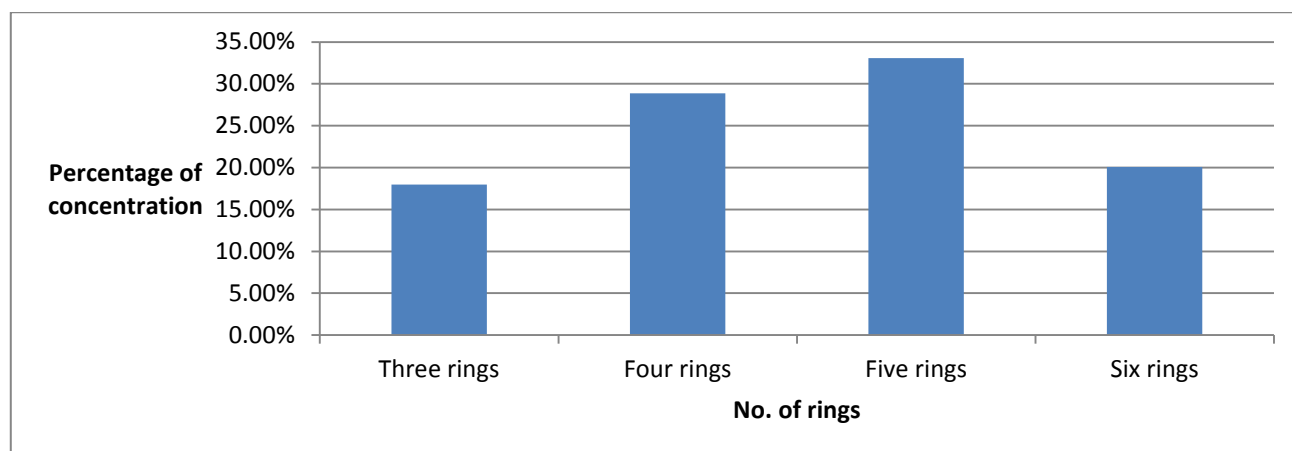


Figure 1: relation between No. of rings with percentage of existence

Conclusion

Ten of thirteen PAHs were detected in soil samples collected from surface soils in Al-diwaneya city. Three compounds are not detected; Fluorene, Anthracite and Benz[a]anthracites, the absence of these compounds may be attributing to biodegradation by microorganism in soil. This study showed that soil sample of site

three is the highest existence of PAHs among other sites. Five fused rings was the highest percentage than three, four and six fused rings of PAHs.

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