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EVALUATION PAHS IN AGRICULTURE SOIL SAMPLES - AL-KHACHEYA SITE SOUTH OF BAGHDAD, IRAQ

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Abstract

Al-Khacheya site south of Baghdad (75km), one of the important agriculture sites, there few of oil wells (currently closed) appears in these fields. In this study, soil and cutting samples were collected from different locations during the period from January to June 2017. HPLC analysis for 16 priority pollutant polyaromatic hydrocarbons (PAHs) were performed, using optimum separation condition on efficient, PAH (50 × 4.6 mm ID), 3µm particle size column from supelco Ltd.

The summation of PAHs concentrations in soil samples ranged from 0.991-0.3226 mg/kg, while the total PAH concentrations in cuttings ranged from 0.14799 to 0.302 mg/kg. ΣPAH concentrations of the seven carcinogenic PAH compounds in soil varied between 0.0991- 0.3226 mg/kg. In terms of composition of patterns in surface water and soil, the PAHs were dominated by four and three rings. The distribution pattern showed marked predominance by low molecular weight compounds. In comparison with ΣPAHs concentrations in other part of the world, the total PAH concentrations of this area were higher than those reported for some urban soils in some regions of the world.

The goal of this work is to study the concentrations distribution of the sixteen PAHs and elements in soil samples from Al-Khacheya site south of Baghdad.

Key words : Polycyclic aromatic hydrocarbons, environmental pollution, Iraqi environment impact.

Introduction

PAHs are a group of chemicals that are formed during the incomplete burning of coal, oil, gas, wood, garbage, or other organic substances, such as tobacco and charbroiled meat. There are more than 100 different PAHs. These chemicals generally occur as complex mixtures (for example, as part of combustion products such as soot), not as single compounds. PAHs usually occur naturally, but they can be manufactured as individual compounds for research purposes; however, not as the mixtures found in combustion products. As pure chemicals, PAHs generally exist as colorless, white, or pale yellow-green solids. They can have a faint, pleasant odor. A few PAHs are used in medicines and to make dyes, plastics, and pesticides. Others are contained in asphalt used in road construction. They can also be found in substances such as crude oil, coal, coal tar pitch, creosote and roofing tar. They are found throughout the environment in the air, water and soil. They can occur in the air, either attached to dust particles or as solids in soil or sediment.

Although, the health effects of individual PAHs are not exactly alike, the following 16 PAHs are considered as a group in this profile :

acenaphthene
acenaphthylene
anthracene
benz[a]anthracene
benzo[a]pyrene
benzo[b]fluoranthene
benzo[g,h,i]perylene
benzo[j]fluoranthene
benzo[k]fluoranthene
chrysene
dibenz[a,h]anthracene
fluoranthene
fluorene
indeno[1,2,3-c,d]pyrene

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phenanthrene

pyrene

These 16 PAHs were chosen to be included in this profile because (1) more information is available on these than on the others; (2) they are suspected to be more harmful than some of the others, and they exhibit harmful effects that are representative of the PAHs; (3) there is a greater chance that you will be exposed to these PAHs than to the others; and (4) of all the PAHs analyzed, these were the PAHs identified at the highest concentrations at National Priorities List (NPL) hazardous waste sites previously reported (Jianwang *et al.*, 2017).

Polyaromatic hydrocarbons (PAHs) are a large group of organic compounds with two or more fused aromatic rings. They have a relatively low solubility in water, but are highly lipophilic. Most of the PAHs with low vapor pressure in the air are adsorbed on particles. When dissolved in water or adsorbed on particulate matter, PAHs can undergo photodecomposition when exposed to ultraviolet light from solar radiation. In the atmosphere, PAHs can react with pollutants such as ozone, nitrogen oxides and sulfur dioxide, yielding diones, nitro- and dinitro-PAHs, and sulfonic acids, respectively. PAHs may also be degraded by some microorganisms in the soil (PAH, 1987).

PAHs are formed mainly as a result of pyrolytic processes, especially the incomplete combustion of organic materials during industrial and other human activities, such as processing of coal and crude oil, combustion of natural gas, including for heating, combustion of refuse, vehicle traffic, cooking and tobacco smoking, as well as in natural processes such as carbonization. There are several hundred PAHs; the best known is benzo[a]pyrene (BaP). In addition a number of heterocyclic aromatic compounds (e.g. carbazole and acridine), as well as nitro-PAHs, can be generated by incomplete combustion (PAH, 1995).

The most important fate processes in soils, especially for the higher molecular weight PAHs are adsorption and biodegradation. These PAHs remain tightly sorbed to soils, and especially the five- to six-ringed PAHs may exhibit a very limited bioavailability to terrestrial organisms based on soil contact or to aquatic organisms based on groundwater-mediated transfer.

Microbial degradation of PAHs in the soil environment is generally the most important process accounting for intermediate to long-term changes in substance levels over time (USEPA, 1990). Resistance to microbial degradation in either soils or water tends to increase with the molecular weight and number of rings, as well. Whereas naphthalene tends to be readily degraded in most situations, PAHs with four, five, or six rings tends to be degraded much more slowly. In general, biodegradation in an aerobic environment occurs much more rapidly than in an anaerobic environment (Neff, 1979). PAHs enter the environment mostly as releases to air from volcanoes, forest fires, residential wood burning and exhaust from automobiles and trucks. They can also enter surface water through discharges from industrial plants and waste water treatment plants, and they can be released to soils at hazardous waste sites if they escape from storage containers. The movement of PAHs in the environment depends on properties such as how easily they dissolve in water, and how easily they evaporate into the air. PAHs in general do not easily dissolve in water. They are present in air as vapors or stuck to the surfaces of small solid particles. They can travel long distances before they return to earth in rainfall or particle settling. Some PAHs evaporate into the atmosphere from surface waters, but most stick to solid particles and settle to the bottoms of rivers or lakes. In soils, PAHs are most likely to stick tightly to particles. Some PAHs evaporate from surface soils to air. Certain PAHs in soils also contaminate underground water. The PAH content of plants and animals living on the land or in water can be many times higher than the content of PAHs in soil or water. PAHs can break down to longer-lasting products by reacting with sunlight and other chemicals in the air, generally over a period of days to weeks. Breakdown in soil and water generally takes weeks to months and is caused primarily by the actions of microorganisms (CSQGPEHH, 2010). The HPLC chromatographic method used to analysis of priority pollutant PAHs were according to EPA methods (U.S. EPA, 1982, 1986, 1990).

The Iraqi environment has been faced a lot of challenges that caused different problems in soil, water and air, which have been reflected in the health and daily life of citizens. This ecosystem during the years, due to its closeness to the town and to the richness of human activities (e.g. industrial, aquaculture and urban activities) have accumulated in sediments both high PAHs and organic matter levels, so the goal of this work is to study the concentrations distribution of the sixteen PAHs in soil samples and water in Badra site south of Baghdad, and to establish data base for the pollutants in Iraq to compare with the medical problems which were recently elevated in Iraq (cancer incidents, cardiovascular diseases, digestion disease, genetic mutation in new born children and allergy disease) compared with the international criteria for evaluation these types of diseases status.

Martials and Methods

Soil and cutting samples were collected during the period from January to June 2017 from different locations in research study field. Samples were collected using PVC container, all samples were transported using cool box to the laboratory for analysis.

High performance liquid chromatography (Shimadzu LC-10 AVP HPLC) technique used to analyze PAHs. De-ionized water was used in the preparation of all solutions.

Sample preparation

For determination of PAH in soil 1 gm of sample were mixed with 1 liter methanol: chloroform (50:50 v/v), agitated for 1 hr, keep the mixture to settle down for 3hr, then decantation the extract and repeated once, collect the two extract, then concentrated the mixture by evaporating the solvent with a stream of liquid N_2 until reach nearly 0.5 ml, then add some of mobile phase to reach 5 ml. The mixture was passed through 2.5 µm disposable filter. Then 50 µl were injected on HPLC column. The concentration for each compound were quantitatively determined by comparison the peak area of the standard with that of the samples.

Results and Discussion

The samples groups were collected in three periods (each two months). Four samples of soil and cuttings were collected each two months and the total groups were 12 samples from Al-Kacheya site.

PAHs, pre-concentrated by applying SPE (solid phase extraction) then gradient HPLC analysis for the 16 priorities Pollutant PAH.

The 1st soil samples were collected in January – February 2017 which included four samples, the results of PAHs as listed in table 1, which indicated that the summation of PAH were between 0.1565-0.1787 mg/kg.

There are no published standards for soil quality in Iraq; hence analysis results are assessed with respect to Dutch Intervention Values (DIVs) for Soil (DMIE, 2009). The DIVs are accepted by the Iraq Ministry of Environment (MoE). Note that of the soil analyses conducted for this study, DIVs are only available for metals and for the sum of 10 PAHs (*i.e.* Naphthalene, Phenanthrene, Anthracene, Fluoranthene, Benzo(a) anthracene, Chrysene, Benzo(k) fluoranthene, Benzo(a) pyrene, Benzo (g,h,i) perylene and Indeno (1,2,3-cd) pyrene).

Table 1 : PAHs (mg/kg), soil samples – 1st group (January – February 2017).

Analysis	**1st Location**	**2nd Location**	**3rd Location**	**4th Location**
Naphthalene	0.0165	0.0172	0.02074	0.0189
Acenaphthylene	0.01687	0.01469	0.01310	0.00974
Acenaphthene	BDL	BDL	BDL	0.0166
Fluorene	0.01124	0.0204	0.01366	BDL
Phenanthrene	0.01187	0.01228	0.02771	0.01547
Anthracene	0.01654	0.01937	0.0471	BDL
Fluoranthene	0.00875	BDL	0.01838	0.01479
Pyrene	0.016221	0.015427	0.01814	BDL
Benzo(a)anthracene	BDL	BDL	BDL	0.02541
Chrysene	BDL	BDL	BDL	BDL
Benzo(b)fluoranthene	BDL	BDL	BDL	BDL
Benzo(k)fluoranthene	0.01651	0.01446	BDL	0.0197
Benzo (a) pyrene	BDL	BDL	0.01021	BDL
Dibenzo (a,h) anthracene	0.0178	0.01633	BDL	0.01954
Benzo (g,h,i) perylene	BDL	BDL	BDL	BDL
Indeno (1,2,3-cd) pyrene	0.02425	0.02574	0.02784	0.02247
Sum of total PAH	0.15655	0.15589	0.1787	0.15848

- PAHs: Measured by SPE (solid phase extraction) pre-concentration and HPLC analysis for the 16 priority Pollutant.
- BDL: Below detected limit.

Table 2 : PAHs (mg/kg), soil samples – 2nd (March-April 2017).

Analysis	**1st Location**	**2nd Location**	**3rd Location**	**4th Location**
Naphthalene	0.01873	BDL	BDL	0.0164
Acenaphthylene	BDL	BDL	BDL	BDL
Acenaphthene	BDL	0.021	0.0187	BDL
Fluorene	0.0169	0.0354	0.0247	0.01754
Phenanthrene	0.0177	0.01927	0.1899	0.01856
Anthracene	0.0289	BDL	BDL	0.0219
Fluoranthene	BDL	0.0310	0.0219	BDL
Pyrene	BDL	0.0155	0.01487	BDL
Benzo(a)anthracene	BDL	BDL	BDL	BDL
Chrysene	BDL	BDL	BDL	BDL
Benzo(b)fluoranthene	BDL	0.01246	0.01428	BDL
Benzo(k)fluoranthene	0.01954	0.0298	0.0194	0.0247
Benzo (a) pyrene	BDL	BDL	BDL	BDL
Dibenzo (a,h) anthracene	BDL	BDL	BDL	BDL
Benzo (g,h,i) perylene	BDL	0.0188	0.0241	BDL
Indeno (1,2,3-cd) pyrene	BDL	0.0118	0.0104	BDL
Sum of total PAH	0.1017	0.1941	0.3382	0.0991

The 2nd set of cutting and soil samples were collected during March to April 2017 from the field which included four samples, the results of PAHs as listed in table 2,

Table 3 : PAHs (mg/kg), soil samples–3rd group (May –June 2017)

Analysis	**1st Location**	**2nd Location**	**3rd Location**	**4th Location**
Naphthalene	0.0210	0.01944	0.0219	0.1627
Acenaphthylene	0.01274	0.01365	0.01354	0.0081
Acenaphthene	BDL	BDL	BDL	0.0166
Fluorene	0.0196	0.0214	0.01877	BDL
Phenanthrene	0.0214	0.03146	0.02871	0.01643
Anthracene	0.0294	0.03194	0.0658	BDL
Fluoranthene	0.01338	BDL	BDL	0.01576
Pyrene	0.01733	0.01684	0.01981	BDL
Benzo(a)anthracene	BDL	BDL	BDL	0.03119
Chrysene	BDL	BDL	BDL	BDL
Benzo(b)fluoranthene	BDL	BDL	BDL	BDL
Benzo(k)fluoranthene	0.01246	0.015789	0.01641	0.02539
Benzo (a) pyrene	BDL	BDL	0.01021	BDL
Dibenzo (a,h) anthracene	BDL	BDL	BDL	0.0121
Benzo (g,h,i) perylene	BDL	BDL	BDL	BDL
Indeno (1,2,3-cd) pyrene	0.02208	0.02914	0.02884	0.02169
Sum of total PAH	0.14799	0.22985	0.22395	0.3026

which indicated highly elevated in the total sum of PAH (it was 0.3382 mg/kg) in sample 3, and reduction in other sample 1and 4, which was 0.1017-0.0991.

The 3rd set of soil samples were collected during May to June 2017, which included four samples, the results of PAHs as listed in table 3, show significant elevated in the total sum of PAHS specially samples 2,3,4 ,the total PAHs were, 0.22985,0.22395 and 0.3026 mg/kg, due to collect the sample from deep place in the field, near oil wells.

Conclusion

Sixteen priority PAHs (consider by EPA as priority PAHs pollutants) in soil were detected using accurate method (HPLC) and comparison the data obtained with the reference values established by Dutch Intervention Values (DIVs) for soil, to estimate the maximum allowable concentration mg/kg for each PAH, in the media under investigation, to estimate the safe media and the extent of polluted media, to let us have to the decision and method of treated and retested to reach the allowable safe concentrations.

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