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POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) AS BIOMARKERS IN THE CONTROLLING HEADQUARTERS, AL-MUTHANNA MILITARY AIRPORT, BAGHDAD, IRAQ

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Abstract

Three stations were chosen on the main controlling site from the Muthanna Military Airport in the center of the capital, Baghdad, with the control site from inside the University of Baghdad for the purpose of comparison. Five replicates collected an environmental sample for each site dominating plants. Samples were prepared and PAH concentrations were determined by gas chromatography / mass spectrometry (GC / MS). Polycyclic aromatic hydrocarbons (PAHs) interactions were shown in all types of plant samples during the quantitative measurement of three types of plants *Eucalyptus camaldulensis*> *Ziziphus spina-christi*> *Morus alba*. The ability of the plant to absorb as a quick step resulting from the absorption of the amount of soil or deposited from the air dust. By comparing the accumulation of PAHs among all species, *Eucalyptus camaldulensis* are observed, as good biomarkers of PAHs pyrene 27 mg/kg which is the highest.

Key word: Polycyclic Aromatic Hydrocarbons (PAHs), Biomarkers, Al- Muthanna military airport – Baghdad

Introduction

Biomarkers in environmental assessment the concentrate mainly on relationships between the division of toxic matter in environment and potential risks of pollutants, in past decades, risk assessment levels of pollutants in the environment have been considered credible because different pollutants can mutually influence their toxic behaviors. Basic main pollutants and chemicals components have a tendency to stick to the environment such as cadmium, lead, mercury or copper, polycyclic aromatic hydrocarbons (PAHs) and others. Minerals in the biotic environment originate from sources of geological processes related to metal fillings geological formations and human resources (Latif, *et al.,* 2013). Primary contaminants cannot be degraded more so they can undergo different reversible changes in belonging depending on the chemical environment (UNEP. 2001). Many elements are necessary for life functions , plants and animals possess different mechanisms for accumulating sufficient amounts of elements from their environment also facilitate the treatment of non-essential minerals (Wang, *et al.,* 2004). Treatment and retention of metals (or any other chemical), environmental pollution and the effects of chemicals on the environment and natural resources have become one of the major global problems (Wuana and Okieimen, 2011). The biological response such as ranging from molecular to cellular and physiological responses to behavioral changes, that can be associated with exposure plants to toxic chemicals or their toxic effects (Hu Lia, *et al.,* 2000). To understand the concept of biomarkers in plants ecosystems, the important aims that identify the changes that had happened in the environmental areas from various sites were chosen from in the controlling headquarters, Al- Muthanna military airport - Baghdad with the following.

1- Detection of polycyclic aromatic hydrocarbons (PAH) in leaf Plants for main stations from in the controlling headquarters, Al- Muthanna military airport - Baghdad to identify the most important sources of elements to identification of health risks according to Potential Ecological Risk Index (RI).

2- Examination of functional groups as biomarker by applying Gas Chromatography Mass Spectrometry (GC/MS).

Materials and Methods

Description and samples collection of this study

Three stations were selected on the basic location from Al-Muthanna military airport in Baghdad in the

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center of the capital Baghdad in the side of Karkh northeast of Baghdad within the coordinates (331924N-442239E).

1- The first site at the beginning of the camp included the corridor entering the military convoys (Station 1).

2- The second site includes the military hospital and service buildings of the middle location (Station 2).

3- The third site is the center of military equipment in final location (Station 3).

4- Al-Jadiriya site inside the College of Engineering in Baghdad University for comparison with our results (Station 4) as a control.

Five replicates were collected environmental sample for dominant Plants in the sites had a long period of years to grow plant samples (*Eucalyptus camaldulensis, Ziziphus spina-christi. Morus alba*).

Preparing Experimental and Analysis:

The samples were collected from the study areas during October in 2019 were taken for each site samples of the plant, surrounding soil and air five replicate samples of each plant leaf were collected, then rinsed thoroughly with deionized water and dried outdoors at room temperature for 3-5 days, then grinded with a mill and sifted with a 1 mm diameter sieve to be ready for analysis. The total samples of the sites were 60 plant samples (WHO, 1996).

Mechanical Extraction PAH of Leaf Plants

Plants *(Eucalyptus camaldulensis, Ziziphus spina-christi, Morus alba*) was performed to extraction by a Soxhlet apparatus. Exhaustive extraction with absolute ethanol was performed using 20g of powdered leaves samples with 200mL of solvent. The ethanol solvent was evaporated by concentrating under vacuum with rotary evaporator at 40°C under reduced pressure. The extract was then filtered through Whitman filter paper. The solvent free ethanol extract was thereafter evaluated the resulting extract was lyophilized and then the extraction yield was calculated (Zhang, *et al.,* 2008), to measured polycyclic aromatic hydrocarbons (PAH) in three types of plants samples were determined using Gas Chromatography-Mass Spectrometer (GC-MS) According (Rossbach, *et al.,* 2007). All analysis was carried out in labs of environment and water directorate/ ministry of science and technology. The gel was filled in a glass column (30 -240 cm length) equipped with a glass flit and a Teflon stopcock about 2 cm of Na_2SO_4 were placed on top of the 17 cm high gel bed. Prior to the first use the column was rinsed with 300 ml of toluene. After application of a sample extract in 0.5-1 mL toluene, a solvent reservoir with toluene was connected to the column without additional pressure, resulting in a flow of approximately 2.5 mL per minute. Fractionation was performed gravimetrically: The first 56g (65 mL) were discarded, the following 45g (52mL) contained the PAH. After a last fraction of 30g (35mL), which was also discarded, the column was ready for the next sample application. The gel permeation chromatography, the second fraction containing the PAHs was concentrated to a volume of about 0.5 mL by rotary evaporation. It then was applied to the second column 1 cm , which had been wet packed with 5g of activated silica gel washed with methanol and dichloromethane, activated for 2 hours at 180°C and 1g of Na_2SO using a mixture of hexane and toluene. This column was rinsed with 40mL of hexane, toluene (4:1) and the equate was collected as one fraction. The column material was discarded after use. After evaporation to a small volume, the samples were transferred to 100 mL. The final volume was adjusted to 20-50 mL, depending on the plant sample type.

Analyzing the compositions using GC-MS device:

The following conditions were used for all types leaf Plants including Column: ZB-5MS Capillary Column (30 m × 0.25mm, I.D. 0.25 µm) , Carrier Gas: UHP Helium , Injection Temperature: 280^{0}C, Detector Temperature: 200 CÚ , Injection Mode: Split , Split Ratio: 5 , Flow Control Mode: Pressure , Injector Pressure: 100 KPa , Total Flow: 11 µl/min , Column Flow: 1.37 µl/min , Linear Velocity: 42.5 Cm/s and Injection Volume: 1 µl (Serdar, *et al.,* 2003a).

Statistical Method

The statistical analysis was performed according to the AOAC Protocol (Thompson, *et al.,* 2006) was assessed using different measures of statistical and coefficient of determination correlation coefficient, mean prediction error concentration of component standard method. The coefficient of determination, r^2, was calculated where N is the total number of paired observations. A value of $r^2 = 1$ indicates 100% precision between the methods.

Results and Discussion

Interferences Polycyclic aromatic hydrocarbons (PAHs) in all types plants samples during quantification

Have been evaluated the PAH in three types of plants by (GC-MS) was used these tests highlighted that the highest value of PAH was found in *Eucalyptus camaldulensis >Ziziphus spina-christi >Morus alba.* The PAH amounts in the samples show tendency to

increase with time passes through the readings, there was indication that PAHs from samples had accumulated on the last column. The mean of the calculated quantities which were near the detection limits in most cases < 0.5 mg/kg. These amounts represented > 0.5 % (IAR, 2008; Ajmi, 2012)of the mean concentration of the plant samples for all compounds recoveries in all types' plants. This indicates the ability of a plant to adsorb as a quick step that can be reversed during reading the device. The surfaces of the leaf of the plant have shown an exceptional ability to trap PAHs on their surfaces where when precipitation occurs, important stages either absorb them into the leaf or keep them on the plant surfaces resulting from the absorption of the amount of soil or It is deposited on it from air dust the environmental factors affecting PAHs transferred from atmosphere to vegetation represented by various factors were shown to be related to the process of PAHs from air to plant, including concentrations of the compounds in the air and its presence gaseous and particle associated temperature and photolysis are important roles in affecting the process of PAHs change from air to plants physicochemical properties, leaf surface morphology, air temperature, and photolysis this corresponds to (ACGIH, 2006; Abdel-Shafy and Mansour, 2016). There are many studies focusing on PAHs to determine the main parameters of pollution correspond to the results of the study such as (Piccardo, *et al.*, 2005; Adamo, *et al.*, 2008; Adamo, *et al.*, 2011; Al-Dabbas and Afaj, 2015). Election frequencies of Pyren were the highest (100%) about 27 mg/kg with Benzo perylene and Dibenzo anthracene. The detection frequencies were the lowest of Pyren in all PAHs at a detection rate of 2% .Results showed that *Eucalyptus camaldulensis* have highest total concentration Pyrene1:1of all samples and 20 mg/kg in *Ziziphus spina-christi* and 17 mg/kg in *Morus alba*, obviously the Its proximity to the site of military equipment and military convoys daily in this study area this is agree with (USEPA, 2009 and 2012). Table (1, 2, 3) showed the average concentrations PHA of all types plant under this study.

Table 1: The average concentrations PAH of *Ziziphus spina-christi*.

PAH of *Ziziphus spina-christi*	mg/kg
Flouronaphthalene	14
Accnaphthylene	15
Fluorene	16
Phenanthrene	17
Anthracene	17
Pyrene	20
Benzo(a)anthracene	22
R^2	1.77%

Table 2: The average concentrations PAH of *Eucalyptus camaldulensis*.

PAH of *Eucalyptus camaldulensis*	mg/kg
Chrysene	22
Pyrene	25
Benzo(k)fluoranthene	25
Benzo(a)pyrene	25
pyrene	27
Dibenzo anthracene	27
Benzo perylene	27
R^2	2%

Table 3: The average concentrations PAH of *Morus alba*

PAH of *Morus alba*	mg/kg
Chrysene	15
Benzofluoranthene	16
Benzofluoranthene	17
Accnaphthylene	15
Fluorene	15
pyrene	17
Anthracene	17
R^2	1.3%

Comparison of PAHs accumulating capability

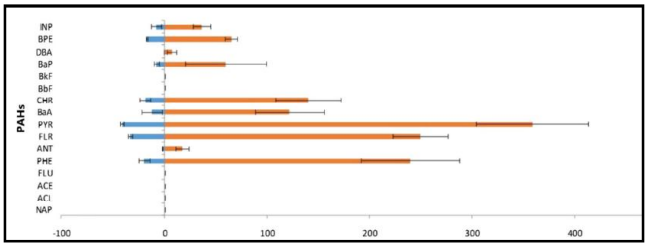

Fig. 1: Accumulating capability of PAHs *Eucalyptus camaldulensis* range between 100, -100.

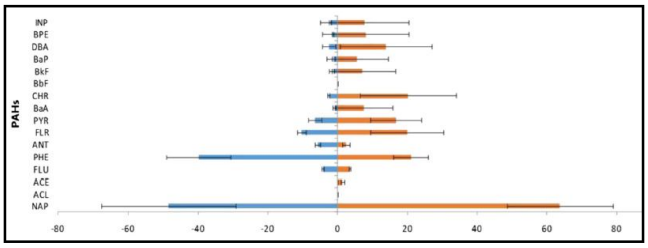

Fig. 2: Accumulating capability of PAHs *Ziziphus spina-christi* range between 20, -20.

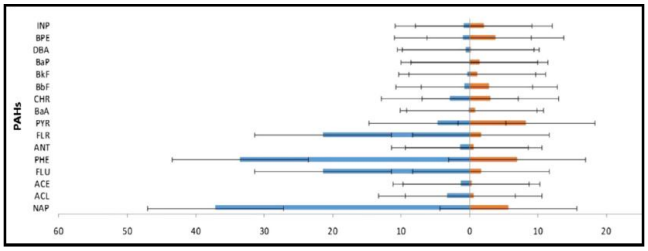

Fig. 3: Accumulating capability of PAHs *Morus alba* between 10, -10.

between all types leaves plants *Eucalyptus camaldulensis, Ziziphus spina-christi, Morus alba* as a good bioindicators of PAHs, differences remain in concentrating various PAHs. As displayed in Fig. 1, 2, 3., the *concentrations Eucalyptus camaldulensis >Ziziphus spina-christi >, Morus* alba leaves. The explanation accounted for this behavior probably is due to the difference in ecological growth of long periods in the study area and ability to tolerate and absorb pollutants on a daily basis, which gain them more opportunities to absorb gaseous PAHs and to accumulate particle bound PAHs and affected by environmental factors like wind or rain which might be attributed to the transfer PAHs from shrub layer or even to the ground (Chaemfa, *et al.,* 2008; Chaemfa, *et al.,* 2009), the difference in leaf properties *Eucalyptus camaldulensis* shown complex network structures which contribute to the trapping of particulates on needles surfaces. Thus, the diffusion of PAHs from the particulates to the inner parts might be facilitated. However, due to the strong interactions of PAHs with the constituent of the cuticle layer PAHs can hardly enter the inner tissue of and can be moved by external environmental factors such as rain or temperature and solar radiation, gaseous PAHs diffuse and accumulate more readily into the inner part this agree with (Boonyatumanond, *et al.,* 2006; Bohlin, *et al.,* 2014). The contrary the other types *Morus alba* leaves which possess an undeveloped cuticle layer this is what the researcher mentioned (Ali, *et al.,* 1993). The total PAH concentration is significantly higher in *Eucalyptus camaldulensis >Ziziphus spina-christi > Morus alba* leaves.

Conclusion

Through the results of the PAHs concentration that have been obtained from analyzed samples were reached of the bioindication environmental and how to transition in ecosystem of the Al- Muthanna military airport – Baghdad. The explanation accounted for this behavior probably is due to the difference in ecological growth of long periods in the study area and ability to tolerate and absorb pollutants on a daily basis , which gain them more opportunities to absorb gaseous PAHs and to accumulate particle bound PAHs and affected by environmental factors like wind or rain which might be attributed to the transfer PAHs from shrub layer or even to the ground , the difference in leaf properties *Eucalyptus camaldulensis* shown complex network structures which contribute to the trapping of particulates on needles surfaces. Thus, the diffusion of PAHs from the particulates to the inner parts might be facilitated. However, due to the strong interactions of PAHs with the constituent of the cuticle layer PAHs can hardly enter the inner tissue of and can be moved by external environmental factors such as rain or temperature and solar radiation, gaseous PAHs diffuse and accumulate more readily into the inner part this agree with (Mumtaz, *et al.,* 1996; Boström, *et al.,* 2002; Ferrari, *et al.,* 2002; Delfino, *et al.,* 2009; Demetriou, *et al.,* 2012). The contrary the other types *Morus alba* leaves which possess an undeveloped cuticle layer. The total PAH concentration is significantly higher in *Eucalyptus camaldulensis >Ziziphus spina-christi > Morus alba* leaves.

Recommendation

Strongly support the more intensive sampling to represent the spatial distribution of the risks of other elements in all Baghdad areas and focus on working spatial information about the idea of the relative risk between variables in environmental and biological factors soil, Air and blood human allows users to evaluate potential policy options and poses better questions to decision makers seeking to protect susceptible populations of PAHs.

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