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Polycyclic aromatic hydrocarbons in intertidal Mudflat in South of Iraq

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Abstract. chosen to collect the sediment sample, three stations were near the Marine water and one station was near the river, total Polycyclic aromatic hydrocarbons (TPHs) were estimated and the results were as following : (TPHs) compounds ranged between (11.6-16.44) $\mu\text{g/g}$ in both stations (2) and (3) but in river station was (6.9) $\mu\text{g/g}$, Polycyclic aromatic hydrocarbons (PAHs) in sediments registered the following data : Acenaphthene was between (N.D -0.796) $\mu\text{g/g}$, Fluorene recorded (N.D -3.353) $\mu\text{g/g}$, Phenanthrene (N.D -0.031) $\mu\text{g/g}$, Anthracene compound was in very high level about (26.653 -26.653) $\mu\text{g/g}$ in sation (1,3), Pyrene (N.D -0.052) $\mu\text{g/g}$, Benzo [a] anthracene (0.227-0.178) $\mu\text{g/g}$ and Chrysene (0--0.061) $\mu\text{g/g}$. Benzo[b]fluoranthene, Fluoranthene and Naphtalene compounds were N.D. The grain size study shown that sediments are classified as silty clay sediments with high percentage of clay between (65-85 %), and also with a high natural moisture content.

Keywords. Mudflat, (TPHs), (PAHs), the grain size.

1. Introduction

Several PAHs have toxic, mutagenic and sometimes carcinogenic characteristic. Even though there are many PAHs studies focus on only a limited number of PAHs, in general only 14 and 20 individual PAH compounds. PAHs classified to two kinds (large and small) according the aromatic rings. Small PAHs are availability in environment as defined by the International Agency for Research on Cancer [1].

Partial combustion of many organic material for example coal, oil and wood produce Polycyclic aromatic hydrocarbons (PAHs) for the environment [2], The main sources of PAHs in surface soils are the dropping PAHs form atmosphere. Several of these PAHs are from close sources, such as refinery industrial activities. Further PAHs are cams far-away sources and have been carried by the air. When PAHs are fall onto the soil, they can become mobile. as their properties to bound with soil particles [3]. PAH transportation in soil particulates by the sorbent with particle size and the pore throat size of the soils [4].

Generally, polycyclic aromatic hydrocarbons (PAHs) are environmentally persistent. Various structures and toxic in some compounds. PAHs enter the environment through various by way and often found as a mixture of compounds [5]. Because of the heavy use of oil the oil spills are a frequent occurrence, particularly in petroleum products, which use in our daily lives, Crude oil is an important



material and the global requirement of petrol expected to soar by 44% over the next two decades, Petroleum refinery effluents (PRE) are composed of different toxic organic compounds with grease [6].

Marian Sediments are deemed as a mirror for the Iraqi castle and an important to reservoir for various pollutants such as polycyclic aromatic hydrocarbons, pesticides and heavy metals and help to transfer of pollutants to aquatic system under the proper situation and also depend on connections between water and sediment [7], (Zuhair et al, 2019) measured the sediment sample from river and marine station on southern Iraq for trace elements. It shows there are no significant differences in the concentrations between stations at $P \geq 0.05$ level and also the geo accumulation index was calculated for trace elements in study area. [8] estimated PAHs in sediment sample from seven station along Shatt AL-Arab estuary and north – west region of the Arabian Gulf the sources of PAHs is both pyrogenic and petrogenic, undoubtedly less by biogenic origin but all ranged in acceptable limit.

[9] study the concentration of PAHs in estuarine station in southern Iraq show that the sources of PAHs in sediment were Petrogenic and pyrogenic.

2. Materials and Methods

2.1. Study Site

Iraqi mudflat is estuarine area located along the southern part of the Iraq coast, despite of the short length of the Iraqi coast (64km) with Kuwait coast about 500 km long coastline and the Iranian coast (2000 km), it represents Iraq's only sea front on the Arabian Gulf [10], four random sediment samples (1,2,3) estuarine sediment samples and (4) river sediment sample were collected by Van Veen grab Sampler and put in aluminum foil paper until reached for lab dried by (Freeze drier Edward-English), Mechanical mortar grinding for sample was discarded using metal sieve about 62 μ bore, than extraction process was don based on the method described by Goutex and Saliot (1980) and by ioc /wmo (1982), by placing 10 g of dried, ground, and transported sediments into the two recovery zones, Use the Soxhlet intermittent extraction device (Heraeus RE6 50D) with a mixture of methanol benzene (1:1) for 24 to 36 hours after which Saponification has been performed For two hours 25ml of water solution for potassium hydroxide methanol was then transported to the separation funnel with the addition of 30ml hexane and was left to stabilize, two layers formed a layer which contain hydrocarbons, The sample was then passed in a chromatography column with a glass-wool, a silica gel, and Al₂O₃ layers, with a layer of anhydrous sodium sulfate 30ml of hexane pass through the column to obtain the aromatic compounds. Last pitcher of the drought and then add 5ml of hexane to make the sample ready to be measured by fluoridation machine (RF.5301 PC Spectrofluorometer Shimadza) for TPHs and use HPLC (Shimadza DGU-20A5R) for determination polycyclic aromatic hydrocarbons. Grain size tests were carried out according to British Standard (BS) 1377, 1990. It was done in engineering geology lab at Marine Science Center in university of Basrah.

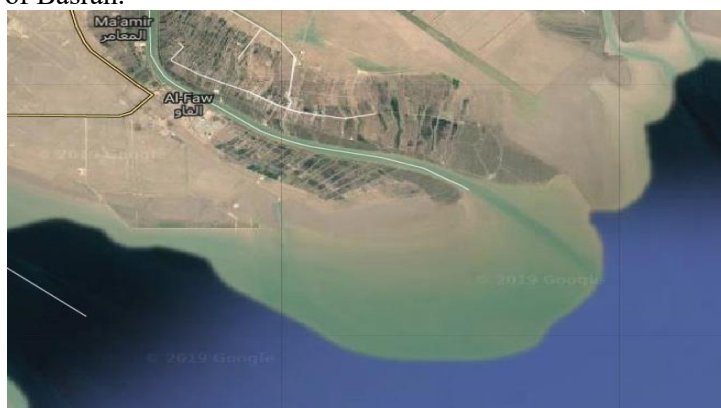


Figure 1. the locations of study area in Basra estuary



Figure 2. Photo shows the mudflat area in the southern of Basrah

3. Results and Discussions

Polycyclic aromatic hydrocarbons were measured with physical and engineering properties and stations (1, 2, 3, 4) for estuarine stations.

3.1. TPHs in sediment

The present study show that the total Polycyclic aromatic hydrocarbons (TPHs) ranged between (11.6-16.44) $\mu\text{g/g}$ see figure (4) and (5) for Marian stations, we can see in river station the concentration was (6.9) $\mu\text{g/g}$. The upper sediment layer about (0.5) cm directly contact with pollutant, the sources of hydrocarbons may came from refinery industrial activities and because of its properties the (TPHs) adsorption On the sediment [11], same result obtain by [8] and (Al-Hejuje et al.,2015)) as well as [9].

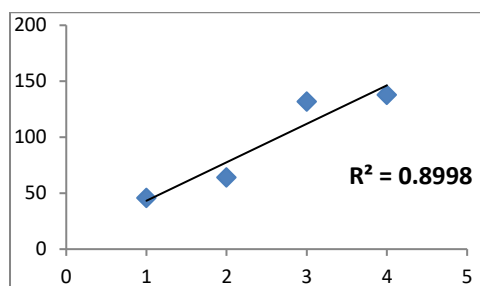


Figure 3. The standard calibration for PAHs

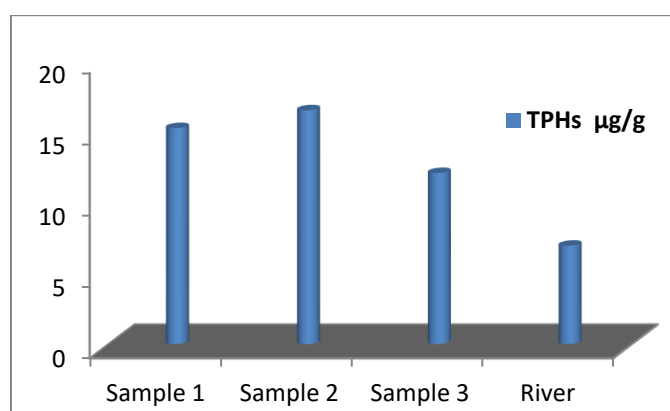


Figure 4. shows the concentration of total polycyclic aromatic hydrocarbons (TPHs) in four Stations of Shatt AL-Arab estuarine

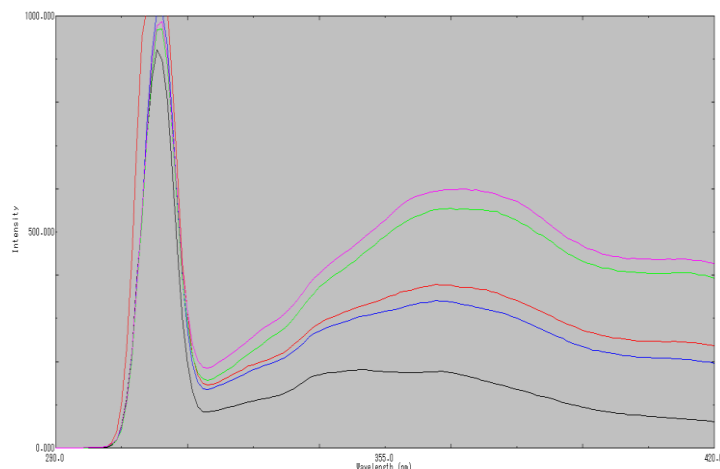


Figure 5. Shows the spectra of the standard for Total polycyclic aromatic hydrocarbons (TPHs)

3.2. Polycyclic aromatic hydrocarbons (PAHs) in sediments

The sixteen polycyclic aromatic hydrocarbons selected as a priority pollutants by the U.S Environmental Protection Agency (EPA) recorded data as the following: Acenaphthene (0-0.796) $\mu\text{g/g}$, Acenaphthene, Fluorene (0-3.353) $\mu\text{g/g}$, Phenanthrene (0-0.031) $\mu\text{g/g}$, Anthracene (26.653 -26.653) $\mu\text{g/g}$ Pyrene (0-0.052) $\mu\text{g/g}$, Benzo [a] anthracene (0.227-0.178) $\mu\text{g/g}$, Chrysene (0--0.061) $\mu\text{g/g}$, unfortunately only total hydrocarbon results have been collected for river sample due to technical difficulties.

Anthracene compound was in very high level about (26.653 -26.653) $\mu\text{g/g}$ in station (1,3), Anthracene is mainly to anthraquinone of days, Crude oil sample which mix with other polycyclic aromatic compounds [12], The simplest aromatic compounds are phenanthrene and anthracene, because of contain three fused aromatic rings. Alternatively, smaller molecules, Naphthalene, which consists of two coplanar six-membered rings sharing an edge, is another aromatic hydrocarbon. [13], and may have different derivative for specialized Uses, like (1-hydroxyanthracene, 2-hydroxyanthracene, homologous to phenol and naphthols and hydroxyanthracene (anthrol or anthracenol) which is pharmacologically active [14]. The main sources for Fluorene compounds is the manufacture of pharmaceuticals, pesticides, pigments and plastic. Phenanthrene comes by manufacture of resins and pesticides. Pyrene use in manufacture of pigments, [15]. sometime PAHs origin from natural sources like bacterial and algal synthesis, petroleum seeps, erosion of sedimentary for rocks consist of petroleum hydrocarbons [16].

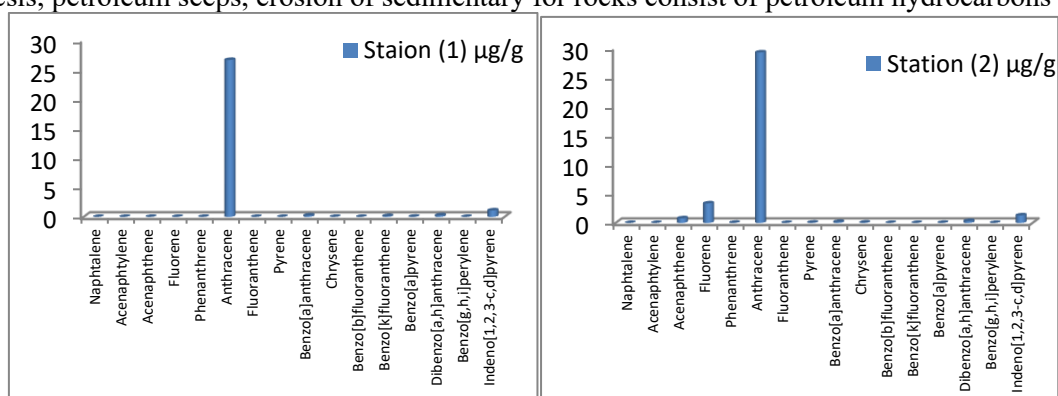


Figure 6. Concentration of PAHs in station (1). **Figure 7.** Concentration of PAHs in station (3)

Table 1. Shows the acceptable limited of PAHs in Marian sediment

polycyclic aromatic compounds	Marian sediment	The present study $\mu\text{g/g}$ Sample (1)	The present study $\mu\text{g/g}$ Sample (3)
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Naphtalene	4.464	0	0
Acenaphtylene	2.99	0	0
Acenaphthene	2.454	0	0.796
Fluorene	1.55	0	3.353
Phenanthrene	1.711	0	0.031
Anthracene	2.99	26.653	29.27
Fluoranthene	0.563	0	0
Pyrene	1.160	0	0.052
Benzo[a]anthracene	2.547	0.227	0.178
Chrysene	1.647	0	0.061
Benzo[b]fluoranthene	1.193	0	0

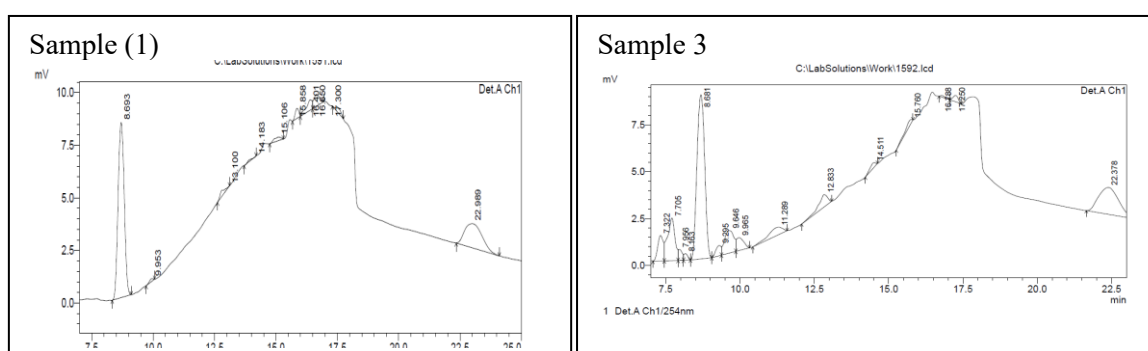


Figure 8. Chromatograms showed the HPLC in some sediment's samples at the stations during the studied periods

3.3. Physical and engineering properties Tests

The sediments texture compounds consist of (sand, silt and clay) and TOC%, the obtund results table (10) show that high level for silt and clay in sediment (60-68) % because of clay tidal flat deposits similar result for [17], when PAHs arrived for soil by any way they are motionless because their non-polar structures slow down them from dissolving in water. But some PAHs are not soluble, particularly the lower molecular weight. Hence, only little of PAHs complete dissolving and turn into the pore water where they are bioavailable. The occurrence of pore water organic colloids can raise the concentrations of PAHs beyond their aqueous solubility since PAHs will be sorbet onto these organic colloids [18].

Table 2. Show the percentage of Sediments texture and TOC% in

Sample No.	Sand %	Silt %	Clay %	TOC %
1	10	60	30	1.27
2	43	42	15	0.76
3	9	69	22	0.86
4	2	68	30	1.05

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