Journal of Ecosystem & Ecography

Abdul and Alshawi, J Ecosys Ecograph 2022, 12:5

Research Article Open Access

Determination of PAHs by GC-Mass in Sediment Mudflat in Iraq

Musa ZJ Salah MS Hassan Abdul[1]* and Zahra Alshawi[2]

[1]*Department of Marine Chemistry, Marine Science Center, University of Basrah, Basrah, Iraq*
[2]*South Oil Company, Basrah, Iraq*

Abstract

The mudflat area in the southern Iraq is untapped and there are few studies about it, this study attempts to determine the concentration of Poly Aromatic Hydrocarbons (PAHs) in the region, addition to determine their sources and assess the quality of pollution by PPI. Total (PAHs) ranged between (89.8-21.9) µg/g dw with mean value (44.62) µg/g dw, among 16 (PAHs) there are 10 of these compounds are dominant in all station as fallow : Benzo (B) the concentration ranged between (14.46-4.743) µg/g dw, Benzo [G,H,I] was (12.5-ND), Benzo [A] Pyrene(7.88-ND), Chrysene (7.85-ND), Fluoranthene (7.31-1.15) µg/g dw, Benzo[A] anthrax (6.14-ND) µg/g dw, Fluorene (2.38-ND) µg/g dw, Indeno (1,2,3 Ca (6.28-1.98) µg/g dw, Pyrene (1.23-ND) µg/g respectively. According to PPI index (PAHs) was between (89.8-21.98) µg/g dw, very high polluted area by (PAHs). The ratio of Ant/(Ant + Phe) show the contamination from Petrogenic origin in station (1) about (1.00-0.275), while the ratio BaA/ (BaA + Chry) recorded the pyrogenic origin in station (1,2,4), A ratio of Fla/ (Fla + - Pyr) shows the station (1, 4) petroleum origin on the other hand the station (2 ,3) derived from coal combustion, finally grain size shows the environmental position of the area and the deposition conditions. In the current study, clay particles are prevalent, ranging from% (15-30) to about% (43-2). Because of the weak alkalinity impact of marine water, TOC recorded a level of % (1.27) near the river station and the lowest value was (6.76)% at the second station. Sewage remains the chief source of TOC in environment.

Keywords: Mudflat area; Fluoranthen, Benzo [A] Pyerene, TOC

Introduction

Oil is the main source of Poly Aromantic Hydrocarbons (PAHs). Besides other sources such as coal, wood combustion, and some usge in the pharmaceutical, agricultural, thermal and chemical industries also there are aromatic compounds in asphalt, tar and electronic parts. There are three types of PAH sources in the environment biological, petrogenic, and pyrogenic which is formed by pyrolysis process when the organic substance be under high temperatures and low concentration of oxygen where the temperature ranged between (350-1200)°C, otherwise PAHs can be formed under low temperatures like PAHs compounds in crude oil. Petrogenic PAHs original from manufacture process of crude oil, transport, storage and oil spill.PAHs are rarely came from biological original these result from decomposition of old plants, animals. PAHs may original from anthropogenic sources which represent by human activity such as automotive emissions, cigar smoke, petroleum product as well as oil spills. PAHs are constantly accumulated from deposited part to the earth as a wet or dry by deposition methods [1]. The octanol-water partitioning coefficient for PAHs are furthermore essential in determining the sorption of PAHs to soils that reflect correlation between the soil and Aqueous solubility. However, the solubility can affect PAH movement in soil. Soil conductivity have similarly a significant effect on PAH movement. Many studies on mudflat area some places on the world try to assessing the PAHs in the sediments of Langkawi, were they used Sediment Quality Guidelines (SQGs) and toxic equivalent factors, samples from jetties and fish farms were taken and they found a significant concentration of PAHs , the sources of PAHs in this sediment likely pyrogenic and petrogenic with low toxicity in the sediment. Sojinu (2010) study examine the sediment from canal and rivers near some oil sites in Niger Delta the results show the dominant compounds were tow-ring PAHs, mostly of PAHs from petrogenic origin came from the incessant oil pipeline outflows in the part [2]. The level of PAHs accumulated by fish captured in the northern part of Gulf has only been calculated in a few cases. One of the most contamination marine environment on the world is the Gulf region. This area product almost two-thirds of the world's refined petroleum this place has shown a lot of development, urbanization, and industrialization, and port areas have become major pollutions in aquatic ecosystem. The level of PAHs accumulated by fish captured in the northern part of Gulf has only been calculated in a few cases. Many locale study in Iraq dell with mudflat area for different pollutant such as trace metal and hydrocarbon like the objective of this paper to evaluate the concentration of PAHs on mudflat area by depending technique (GC-Mass) [3].

Materials and Methods

Sediment sampling

Four different stations located in south part of Basra- Iraq (Mudflat area) in 2019, which covered totally by tidal of the Gulf water. They look like barren regions, no life except some organism such as mudskipper Figure 1 and Table 1. Four unplanned sediment samples (1, 2, 3) for Marian areas and fourth samples are estuarine sediment near the river (Shat AL-Arab), all samples were collected by Van Veen grab Sampler. The sediments were put in plastic container and shipped to the laboratory under frozen condition. The sediments were spread on aluminum foil paper for drying, then mechanical mortar was used to grind the samples after that, sieving by metal sieve about 62 µ bore to be ready for extraction and analyses [4].

The extraction method was done according to the technique described by Goutex and Saliot (1980) and by ioc/wmo (1982), 20g of dried ground of sediments put into the two recovery zones, Use the

***Corresponding author:** Musa ZJ Salah MS Hassan Abdul, Department of Marine Chemistry, Marine Science Center, University of Basrah, Basrah, Iraq, E-mail: research.vlsrc@gmail.com

Received: 16-Mar-2022, Manuscript No: jee-22-57528, **Editor assigned:** 17-Mar-2022, PreQC No: jee-22-57528(PQ), **Reviewed:** 30-Mar-2022, QC No: jee-22-57528, **Revised:** 2-May-2022, Manuscript No: jee-22-57528(R), **Published:** 9-May-2022, DOI: 10.4172/2157-7625.1000331

Citation: Abdul MZJSMSH, Alshawi Z (2022) Determination of PAHs by GC-Mass in Sediment Mudflat in Iraq. J Ecosys Ecograph 12: 331.

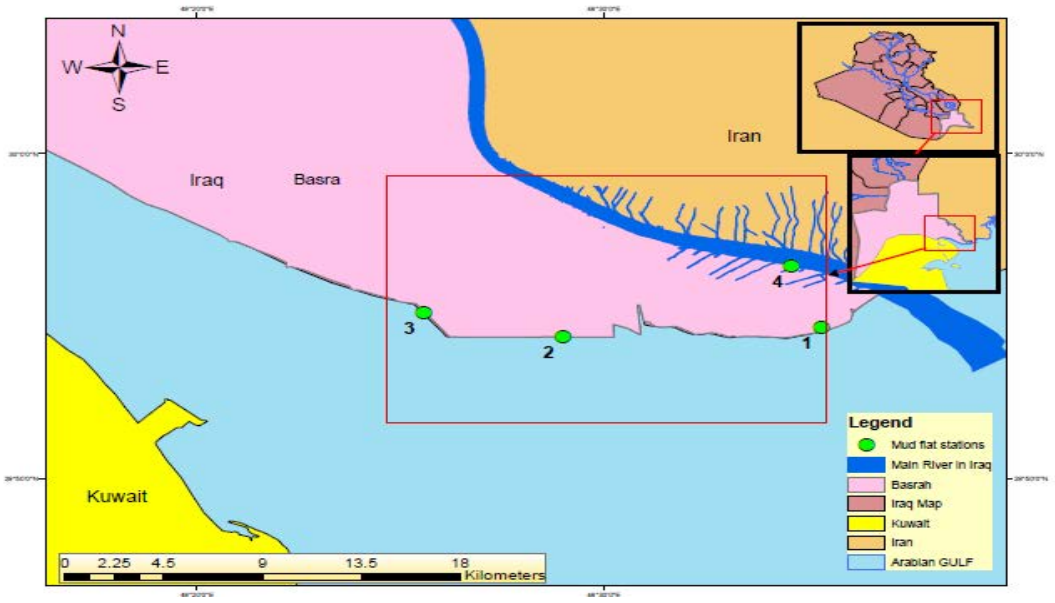
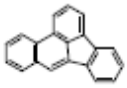
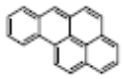
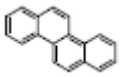
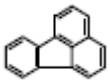
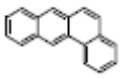
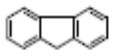
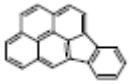
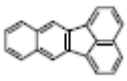


Figure 1: Map showing the sample station.

Table 1: Dominant PAHs in four stations in few Island (Basrah).

Dominant PAHs compounds	Structure	St.1 (µg/g dw)	St.2 (µg/g dw)	St.3 (µg/g dw)	St.4 (µg/g dw)
Benzo[B]Fluoran		14.468	9.258	11.119	4.743
Benzo[G,H,I]		12.504	2.498	ND	4.914
Benzo[A]Pyrene		7.881	5.694	1.995	ND
Chrysene		7.854	1.788	ND	1.758
Fluoranthene		7.312	6.011	1.857	1.154
Benzo[A]anthrac		6.148	2.984	ND	1.074
Fluorene		2.386	1.198	2.106	ND
Indeno(1,2,3-Ca)		1.981	2.047	6.289	3.962
Benzo[K]Fluoran		1.921	0.917	5.752	3.155
Pyrene		1.235	1.159	ND	1.178

Soxhlet intermittent extraction device described by (Heraeus RE6 50D) using a mixture of methanol benzene (1:1) for (24-36) hours after that Saponification process has been done for two hours by using (25 ml of water solution for potassium hydroxide methanol) then transported to the separation funnel with adding 30 ml of hexane and keep on to stabilize. One of the two layers formed contains hydrocarbons. The final sample passed in a chromatography column contains glass-wool, a silica gel, and Al_2O_3 layers with a cover of anhydrous sodium sulfate. About 30 ml of benzene added to the column to get the aromatic compounds. The sample was kept for the drying and then added 0.1ml of hexane to make the sample ready to be measured by GC Mass [5].

GC Mass Condition

A MSD GC Mass Spectrometer Agilent 5977 A MSD, Mass Hunter GC/MS Acquisition software, and Mass Hunter qualitative program, Ion Source Temp, 230°C, Quad temperature 150°C, Interface Temp, (MSD Transfer Line) 290 C, Solvent Cut Time: 4.00 min., Start Time: 4.00 min., End Time: 45 min, ACQ Mode: Scan, Scan Speed: 1562 (N2) ,Start m/z: 40, End m/z: 700. The condition as follow Column Oven Temp. initial (40°C), hold 5 mint, Rate10 c/min, final temp 300°C to end run, Injection Temp. 290°C, Injection Mode: pulsed Splitless, Flow Control Mode: constant flow Pressure: 7.0699 psi, Total Flow: 19 ml/min. Colum Flow: 1 ml/min. Purge Flow: 3 ml/min. Injection volume 1uL, Column type, HP-5MS 5% phenyl methyl siloxane 30m × 0.25 × 0.25 mm. Grain size tests were carried out allowing to British Standard (BS) 1377, 1990. The work done in engineering geology lab of Marine Science Center in university of Basra [6].

Results and Discussions

Incomplete combustion is the principal cause of PAHs. Natural, carbon, oils and timber, for example. PAHs don't exist chemically synthesized for commercial applications. However, for a lot of PAHs, there are a few businesses uses. They are used mainly as intermediaries in medicinal, industrial, photographic, fiberglass, greasing and other chemicals industries. 16 Poly Aromatic Hydrocarbons were estimate in four stations, the results were show there some compounds appear as dominant in four stations [7].

GC-MS Identification of PAHs

The total concentration of PAHs ranged between 89.80 µg/g dw to 21.98 µg/g dw. With a mean concentration of 44.625 µg/g dw, the sources of PAHs in nature are Pyrogenic PAH which comes from incomplete combustion of organic compounds such as fuels and biomass, the second sources of PAHs are Petrogenic PAH usually facilities with oil refinery and biogenic PAH mean sources result from changing of chemical and biological of organic substance in nature. Arabian Gulf is considered as perhaps the most contamination marine biological systems on the planet. Just about, 66% of the world's demonstrated oil saves are situated in the Arabian Gulf. This area has gone through significant turn of events, urbanization and industrialization; port regions have become the significant wellspring of contamination in marine conditions. The assurance of PAHs levels aggregated by fish got from the Northern Arabian Gulf has been restricted. To guarantee the strength of the seaside waters around the Iraqi marine Inlet Arabian Gulf, there is a need to embrace reasonable checking programs [8].

Dominant PAHs compounds

Tenth of polycyclic aromatic hydrocarbon were recorded as a dominant compounds in four station samples Figure 2 and Table 2 the highest concentration was Benzo [B] Fluoran (14.468 µg/g dw),

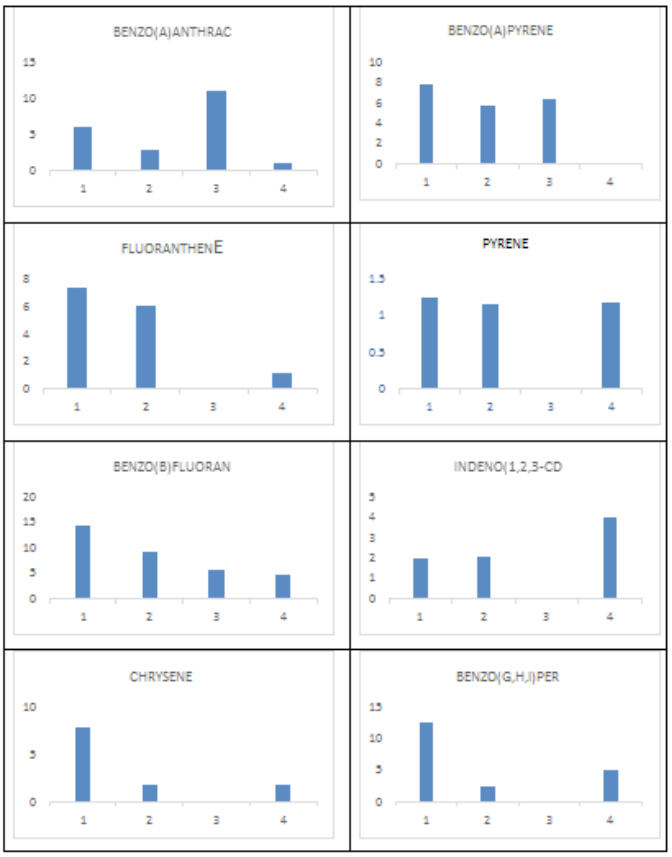


Figure 2: Different recordings of chemical compounds.

Table 2: Shows PAHs Pollution Index (PPI).

(0-0.1 µg/g)	low
(0.1 -1µg/g)	moderate
(1-5 µg/g)	high
(> 5 µg/g)	very high

in station 1 near to the marine area this area influence with big Iraqi petroleum export (Basrah port). Benzo [A] pyrene reached to sediment by discharging to the river with wastewater special that came from industrial sewage, which is carcinogenic according to (IARC, 2009), Fluoranthene, Indeno (1, 2, 3-Ca and Benzo [K] Fluoran recorded in four stations respectively. similar result recorded by Dong (2021) in the study of southern Kaohsiung Harbor industrial port in Taiwan widely polluted by industrial urban Sewage using GC Mass. The main sources of Pyrene is automobiles produce about (1 µg/Km). Pyrene recorded (1.235-1.159-1.178) in stations (1, 2, 4) whereas ND in station 4, Pyrene of characteristic and anthropogenic sources and was represented one of the harmful, mutagenic Polycyclic Aromatic Hydrocarbons (PAHs) recorded as toxic [9].

PAH Pollution Assessment (PPA) index

PAHs Pollution Index (PPI) by using the characterize of sediment quality was suggested by Baumard (1998):

In view of this grouping, PAHs in Iraq mudflat were (89.8-21.98 µg/g dry weight) could be considered as very high polluted with PAHs. In a few cases, it has additionally been shown that some of the PAH proportions are probably going to exaggerate the commitment of pyrogenic PAH to add up to PAH in silt tests in view of co-event of

numerous PAHs in both pyrogenic and petrogenic sources [10].

Generally, a ratio of Ant/ (Ant+Phe) < 0.1 suggests a pollution with petroleum origin, while a ratio > 0.1 indicates a dominance of combustion Table 3 shows the ratio between Ant/(Ant + Phe) in all stations in the present work , station (1) appear Petrogenic PAHs origin about (1.00-0.275). Yunke (2002) suggested that BaA/ (BaA + Chry) ratio < 0.2 indicates petrogenic sources, a ratio between 0.2 and 0.35 indicates a mixed origin, and a ratio > 0.35 implies pyrogenic sources the result in Table 4. We can see the pyrogenic origin in stations (1, 2, 4). A ratio of Fla/ (Fla + - Pyr) < 0.4 is consistent with petroleum inputs; a value between 0.4 and 0.5 indicates liquid fossil fuel (vehicle and crude oil) combustion; and a ratio > 0.5 grass, wood, or coal combustion however the Table 5 shows the two stations 1and 4 origin from petroleum inputs while two stations 2 and 3 came from coal combustion. All these ratios were distinguished between samples containing petrogenic or pyrogenic PAHs.

Grain size

The size of particles is directly dependent on the type of environmental setting, transporting agent, length and time during transport, depositional conditions, and hence it possesses significant utility as an environmental proxy. Grain size examination is a major instrument for grouping unconsolidated materials and silt, sedimentary rocks, and sedimentary conditions. Quantitative examination of the rates of various particulate sizes yields quite possibly the most central actual properties of clastic silt and sedimentary rocks.

Table 3: Shows the ratio of Ant/(Ant+Phe).

PAHs	Station 1	Station 2	Station 3	Station 4
Ant	1.000	0	0	0
Phe	2.626	0	0	0
Ant/ (Ant+Phe)	0.275	0	0	0
The Origin	Petrogenic	-	-	-

Table 4: Shows the ratio of BaA/(BaA+Chry).

PAHs	Station 1	Station 2	Station 3	Station 4
BaA	6.148	2.983	0.000	1.071
Chry	7.854	1.711	0.000	1.758
BaA/ (BaA+Chry)	0.4	0.6	0	0.378
The Origin	Pyrogenic	Pyrogenic	-	Pyrogenic

Table 5: Shows the ratio of Fla/(Fla+- Pry).

PAHs	Station 1	Station 2	Station 3	Station 4
Fla	7.312	6.01	1.857	1.154
Pyr	1.235	1.154	0.00	1.178
Fla /	0.4	0.6	0	0.378
(Fla+Pyr)	0.855	0.839	1	0.494
The Origin	petroleum inputs	Coal combustion	Coal combustion	petroleum inputs

Table 6: The percentage of Sediments texture and TOC% in four stations in mudflat area.

Sample No.	Sand %	Clay %	Silt %	TOC %
Station1	10	30	60	1.27
Station 2	43	15	42	0.76
Station 3	9	22	69	0.86
Station 4	2	30	68	1.05

Conclusion

According to the particle size fraction in all stations the Clay fraction was dominant ranged between (15-30)% , whereas, the send was (2-43)% Table 6 this percentage revealed weak acid, neutral and alkaline reaction, TOC levels in this study were (0.76-1.27)%. The highest was in station near river, anthropogenic waste conceded the main sources of TOC while the lowest value was in station 2 about (0.76%) (mudflat Marian area) receiving less sewage. AI-Manssory (2003) determined five trace metals pollutant the sediment in five station in the northern of Shatt Al P-Arab River and it is estuary during (1997-1998). They found high level of Ni reflected the contamination by hydrocarbon substance, similar study done by Abaychi and Dou Abal (1985), Al-Khafaji (1997) and Al-lmarah (1998) done on this area.

Acknowledgement

I would like to thank my Professor for his support and encouragement.

Conflicts of Interest

The authors declare no conflict of interest

References

1. Abaychi JK, Dou Abal AA (1985) Trace metals in Shatt Al-Arab River, Iraq. Water Research 19: 457-462.
2. Ogunfowokani AO, Subiojo OI, Fatoki OS (2003) Isolation and determination of polycyclic aromatic hydrocarbons in surface runoff and sediments. Water Air and Soil Pollution 147: 245-261.
3. Al-lmarah FJM, Al-Khafaji BY, Moharned ARM (1998) Trace metals in waters, sediments and fishes from Northwest Arabian Gulf. Bull Nat Inst Occanogr Fish A.R.E 24: 403-416.
4. Al-Khafaji BY, Al-lmarah FJM, Mohamed ARM (1997) Trace metals in water, sediments and green black Mallet (*Liza Subviridis*, *Valencielles*, 1836) of the Shatt Al-Arab Estuary, NW Arabian Gulf *Marina Mesopotamica* 12: 7-23.
5. Baumard P, Budzinski H, Garrigues P, Sorbe JC, Burgeot, T, et al. (1998) Concentration of PAH in various marine organisms in relation to those in sediments to trophic level. Mar Pollut Bull 36: 951-960.
6. Baumard P, Budzinski H, Garrigues P (1998) Polycyclic Aromatic Hydrocarbons (PAHs) in sediments and mussels of the western Mediterranean Sea. Environ Toxicol Chem 17: 765-776.
7. Cheng-Di D, Chih-Feng C, Chiu-Wen C (2012) Determination of Polycyclic Aromatic Hydrocarbons in Industrial Harbor Sediments by GC-MS. Int J Environ Res Public Health 9: 2175-2188.
8. Nasher E, Heng LY, Zakaria Z, Salmijah S (2013) Assessing the Ecological Risk of Polycyclic Aromatic Hydrocarbons in Sediments at Langkawi Island, Malaysia. The Scientific World Journal 13.
9. López GI (2017) Grain size analysis. Encyclopedia of Earth Science Series Encyclopedia of Geoarchaeology, Allan S Gilbert Springer 341-348.
10. Li G, Xia X, Yang Z, Wang R, Voulvoulis N (2006) Distribution and sources of polycyclic aromatic hydrocarbons in the middle and lower reaches of the Yellow River, China. Environ Pollut 144: 985-993.